ELECTRON BEAM TECHNOLOGY FOR THE DESTRUCTION OF PERFLOUROOCTANOIC ACID AND PERFLUOROOCTANE SULFONATE IN SOIL AND WATER SAMPLES

A Thesis

by

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ABSTRACT

Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) are two of the most biopersistent and bioaccumulative toxins in our environment today. The EPA has listed them as potential human carcinogens and has set an advisory limit for these chemicals of 70 ppt in water. Research has shown that advanced oxidation processes and ionizing radiation have had success in breaking down these chemicals. This study aims to show the efficacy of one of these processes, electron beam (eBeam) technology, in breaking down PFOA and PFOS. Building on past research and existing work done at the Texas A&M National Center for Electron Beam Research, two major studies were designed to elucidate the dose and conditions needed to facilitate the complete breakdown of these chemicals.

Based on a review of literature, the first study examined the breakdown of PFOA and PFOS at relatively low doses (10 kGy and 50 kGy) with and without chemical amendments ($NaHCO_3$, $NaNO_3$, and pH 13). The results showed that 50 kGy with amendments was the optimal treatment for complete breakdown of PFOA in all matrices, but not for PFOS. Based on these results, a second study focused on the breakdown of PFOS at much higher doses (500 kGy and 2000 kGy) was designed. This study showed that the optimal conditions for complete breakdown PFOS were 2000 kGy and high pH in lab-spiked water and sand samples. In investigation derived soil samples, complete breakdown of PFOS was achieved at the same dose with a low moisture content and high pH. Future studies should focus on the effectiveness of the conditions

tested at 2000 kGy on a variety of field samples, as well as elucidating the breakdown mechanisms of PFOA and PFOS when subjected to eBeam technology.

DEDICATION

This thesis is dedicated to Robert Bilott, the Tennant family, and all others without whom the field of PFAS remediation would not exist. Thank you for your persistence and faith.

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Contributors

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Sample analysis in Chapters 3 and 4 was performed by Dr. Cory Klemashevich and Smriti Shankar of the Integrated Metabolomics Analysis Core at Texas A&M University. Additional commercial analysis was performed by SGS-AXYS in British Colombia, Canada. Dr. Mingbao Feng of the School of Public Health contributed to experimental design, sample extraction, and data analysis. Emily Brorman (Senior, Biomedical Sciences) assisted in sample extraction as an undergraduate research scholar at Texas A&M University.

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All other work conducted for the thesis was performed by the student independently.

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NOMENCLATURE

PFASs: Perfluorylalkyl Substances
PFOA: Perfluorooctanoic acid
PFOS: Perfluorooctane sulfonate
PFBA: Perfluorobutanoic Acid
PFBS: Perfluorobutane sulfonate
POPs: Persistent Organic Pollutants
GAC: Granular Activated Carbon
eBeam: Electron Beam
e^-_{aq}: Aqueous Electrons
AFFFs: Aqueous Fire Fighting Foams
ECF: Electrochemical Fluorination
TFE: Tetrfafluoroethylene
BDE: Bond Dissociation Energy
CDC: Center for Disease Control
EPA: Environmental Protection Agency
AE: Anion Exchange
PWT: Plasma-based Water Treatment
LINAC: Linear Accelerator
MeV: Million electron volts
kW: kilowatts
PPE: Personal Protective Equipment
DUR: Dose Uniformity Ratio
HPLC: High-Performance Liquid Chromatography
kGy: Kilograys
SPE: Solid Phase Extraction
LC-MS/MS: Liquid Chromatography-Tandem Mass Spectrometry
IMAC: Integrated Metabolomics Analysis Core
IDW: Investigation-Derived Waste

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CHAPTER I: INTRODUCTION

Since the first publication on the widespread distribution and bioaccumulation of Perfluorooctane Sulfonate (PFOS) in 2001,[1] there has been a near-constant influx of data regarding the toxicity and persistence of these manmade chemicals called Per- and Polyfluorylalkyl Substances (PFASs). PFASs have been associated with a number of adverse health effects in both humans and animals when ingested in toxic amounts,[2] including but not limited to low birth weight,[3] high blood pressure,[4] and pancreatic and liver tumors in rats.[5] Among this expanding and still relatively uncharacterized and unquantified class of chemicals are two 8-carbon molecules; Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS). These large, amphiphilic molecules (meaning the molecules are made up of both hydrophobic and hydrophilic structures) are resistant to degradation and most environmental remediation technologies [6] and are therefore characterized as Persistent Organic Pollutants (POPs). Their amphiphilic nature and the strength of the carbon-fluorine bond (116 kcal/mol) in these compounds makes traditional contaminant removal methods in water and soil ineffective.[7,8] Therefore, a significant need for PFAS remediation technologies exists.

Of late, there has been a heightened focus of ongoing research on removal technologies such as Granular Activated Carbon (GAC) and ion exchange resins. Degradation technologies such as plasma-based methods,[3] and ionizing radiation technologies such as gamma irradiation[9] and electron beam irradiation are now gaining increased attention.[10] Electron Beam (or eBeam) technology, an ionizing radiation technology utilizes highly

energized electrons generated using electron accelerators. These electrons, on making contact with the target material can cause direct or indirect damage to bacterial DNA and chemicals.[11,12] When electrons interact with water, the following oxidative/reductive radical species are formed:

$$0.7H_2O \xrightarrow{Ionizing\ Radiation} [0.27]e^-_{aq} + [0.28]\cdot OH + [0.06]\cdot H + [0.07]H_2O_2 + [0.27]H_3O^+ + [0.05]H_2 \quad (1)$$

Equation (1) shows the amount of each radical species produced per 10 eV of energy absorbed by water.[13] As PFASs are highly oxidized, radical species with high oxidation potential such as ·OH are unlikely to damage the compounds themselves (although they do have the ability to oxidize organic compounds in field samples that would otherwise interfere with the reaction).[3] The radical species of importance for the breakdown of PFOA and PFOS are the aqueous electrons (e^-_{aq}), which have a high reduction potential and are thought to perform reductive dehalogenation, during which PFASs are destroyed through defluorination via a single-electron transfer with fluorine atoms on PFAS molecules.[14]

The goal of this research project was to conduct experiments investigating the efficacy of eBeam technology to break down PFOA and PFOS and determine the dose and conditions optimal for maximum breakdown. This was achieved through two distinct studies: Low dose (10 kGy-500 kGy) and high dose (500 kGy-2000 kGy).

CHAPTER II: REVIEW OF LITERATURE

Perfluorylalkyl Substances (PFASs)

Origin of PFASs

PFASs were originally discovered and synthesized during the Manhattan Project in the 1940s.[15] The strength of the carbon-fluorine bond and the amphiphilic nature (solubility in both water and lipids) of the molecules were eventually utilized to make products such as non-stick coating for cookware (Teflon™ manufactured by DuPont), fabric protectants (Scotchgard™ manufactured by 3M), and Aqueous Fire Fighting Foams (AFFFs). After years of toxicology testing, 3M entered into a voluntary agreement with the EPA to phase out PFASs as they were a confirmed animal carcinogen and a potential human carcinogen.[16] However, as Dupont continued to dispose of PFAS waste into water systems such as the Ohio River, PFASs (primarily PFOA and PFOS) began to spread throughout the United States.[17] The contamination of this single watershed led to the spread of the chemicals into surrounding ecosystems, including soil, agriculture, livestock, and native flora and fauna.[18–20] This sequence of events created a domino effect which resulted in PFASs existing in the blood of the vast majority of the human population as of 2020.[21]

There are two primary methods of production for PFASs: Electrochemical Fluorination (ECF) and Telomerization. ECF involves the complete replacement of hydrogen atoms with Fluorine atoms on the starting organic material.[15] This is

accomplished first by dissolving the starting material in anhydrous HF.[22] The dissolved organic material is then fluorinated at the anode of an electrochemical cell. The entire reaction is commonly referred to as the Simons process.[23] The Simons process is visually represented in Figure 1 below):

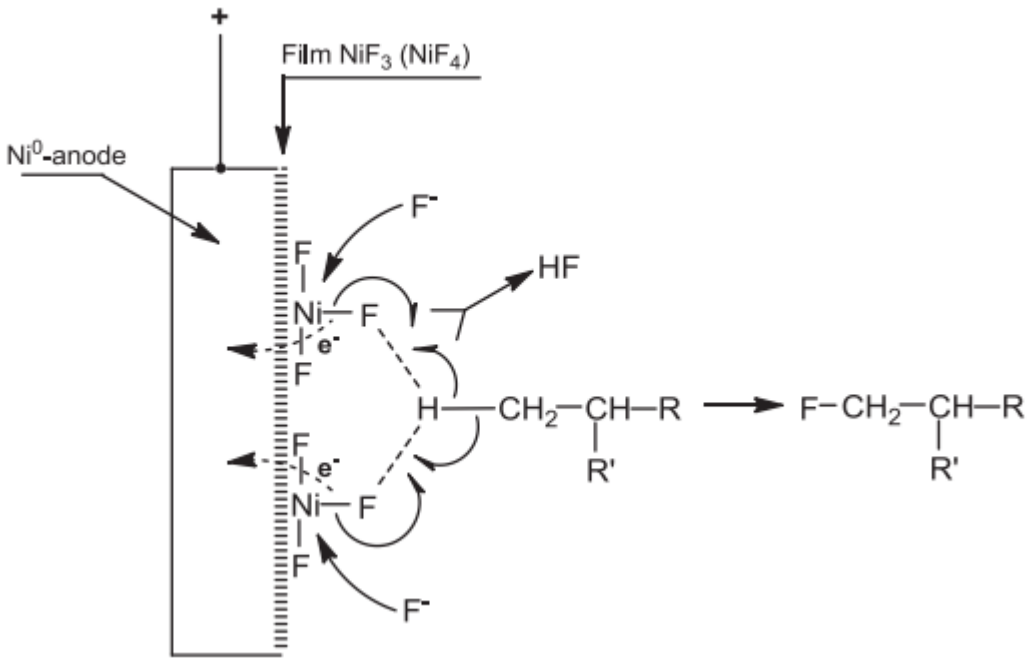


Figure 1. Simmons process of electrochemical fluorination using nickel anodes Reprinted from Ignat'ev 2017

The other primary method for producing PFASs is a process called Telomerization. The first step of the reaction involves two molecules: a telomer (a polymer consisting of a carbon chain completely saturated with non-hydrogen atoms),[24] which is always a perfluoroalkyl iodide (CF_3I); and a taxomer (a polymerizable molecule),[25] which is tetrafluoroethylene, or TFE (C_2F_4).[26] The catalysts for this reaction are historically organic peroxides, which are used in the initiation step to produce the radical species needed for chain propagation.[27] This process produces the intermediate

compounds known as fluorotelomers, which are now included in the screening of PFAS contaminants.[28] The principal steps of telomerization are described in Equation (2):

Initiation: $CF_3I + C_2F_4 \rightarrow CF_3\bullet + I\bullet$ (2)

$CF_3\bullet + CF_2 = CF_2 \rightarrow CF_3CF_2CF_2\bullet$

Propagation: $CF_3CF_2CF_2\bullet + CF_2 = CF_2 \rightarrow CF_3CF_2CF_2CF_2CF_2\bullet$

Transfer: $CF_3CF_2CF_2CF_2CF_2\bullet + CF_3I \rightarrow CF_3CF_2CF_2CF_2CF_2I + CF_3\bullet$

Termination: $2CF_3\bullet \rightarrow CF_3CF_3$

PFASs still in production today continue to be synthesized via either ECF or Telomerization. Although PFOS and PFOA were voluntarily phased out in the early 2000s, many chemicals in this class are still currently in production.[29]

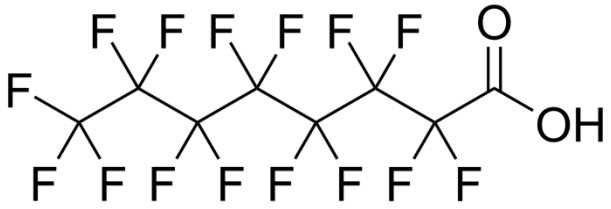
Structure and Chemistry

The chemical structures of PFASs such as PFOS and PFOA are unique for several reasons: the chemical properties of elemental fluorine, the strength of the fluorine-carbon bond, and the amphiphilic nature of the molecules.

Fluorine is a highly reactive halogen with a molecular weight of 18.998 g/mol. Fluorine is also the most electronegative element on the periodic table, and therefore easily attracts pairs of bonding electrons. Furthermore, fluorine has an electron affinity of 83.5 kcal, which refers to the amount of energy released when an electron is added to fluorine to form a negative ion. However, it also has an extremely high ionization energy (401.5 kcal/mol), meaning a large amount of energy is needed to remove an electron

from fluorine in gaseous form.[26] All of these properties form an element that is extremely receptive to covalently bonding to atoms such as Carbon, and once bonded, are very difficult to remove.

The carbon-fluorine (C-F) bond is often referred to as the strongest bond in organic chemistry.[30] This covalent bond shortens in length as more fluorine is added to a carbon, thereby increasing its strength.[31] As the hydrophobic tails of PFOS and PFOA (Figure 2) are comprised completely of fluorine covalently bonded to carbon, these chains have incredibly high Bond Dissociation Energies (BDE), with a fluorocarbon chain (CF_3CF_2—$(CF_2CF_2)_n$) having a BDE of 371.8 kJ/mol.[32] Additionally, the relatively small atomic radius of fluorine covalently bonded to carbon (0.72 Å) allows for the fluorine atoms to completely shield the carbon atoms and bonds without introducing steric hindrance.[26] Paired with the previously discussed properties of fluorine itself, the near-unbreakable nature of the C-F bond makes PFASs extremely stable in almost any environment.



The carboxylic acid functional group of PFOA forms the hydrophilic head of the molecule. In PFOS, this functional group is replaced by sulfonate

Covalently bonded fluorocarbon chain comprises the hydrophobic tail of PFOA

Figure 2. Chemical structure and functional description of Perfluorooctanoic Acid (PFOA)

The amphiphilic nature of PFASs is defined by their having a hydrophobic/oleophobic fluorocarbon tail and a functional group serving as the hydrophilic head (Figure 2).[26] In a solution that contains both water and organic solvents, the hydrophobe also acts as the lyophobe (repels solvated organic molecules). In solution, the hydrophilic functional head will orient itself towards water molecules, with the fluorocarbon tail facing away.[33] Since the functional groups of PFOS and PFOA are hydrophilic and the tails hydrophobic, they persist in water systems without fully dissolving and can be carried long distances.[34] This incredibly versatile structure significantly contributes to the biopersistence and stability of PFASs.

Toxicity

The question of whether PFASs are toxic to human and animal health has been investigated at length by both the producers of these chemicals as well as by government and academic researchers. In animals, PFOA and PFOS are confirmed carcinogens,[35] however, they are still classified as suspected carcinogens in humans.[36] PFOA and PFOS have both been confirmed to cause several other adverse health effects in humans, including but not limited to: high blood pressure, thyroid disruption, low infant birth weight, and physical deformities in newborns.[2,37,38] Additionally, PFOA and PFOS have long half-lives and resist breakdown in humans.[39] This leads to bioaccumulation of PFASs, which collect in the liver, lung, brain, stomach, and many other organ tissues (varies by type of PFAS most prevalent in the region).[40] The most prevalent and most studied health effects from PFAS ingestion in humans are: thyroid disruption, high blood pressure, birth defects, and suspected carcinogenicity.[37,41] Studies concerning thyroid

disruption exceed 400, and several robust studies made links between PFAS exposure and abnormal thyroid activity.[42] Lewis et al. reported on data provided by the Center for Disease Control representing a majority of the US population, which saw a significant positive correlation between PFAS exposure and increased thyroid function.[43] Shrestha et al. similarly reported that fT4 and T4 (hormones commonly used as a benchmark to measure thyroid function) increased with increasing exposure to PFOS and PFOA in elderly patients surveyed in areas adjacent to the Hudson River in New York State.[44] The same study suggested that PFAS exposure is a prevalent health risk as even a small change in thyroid activity can have serious effects on cognitive function.

Several studies representative of various target populations (young adults 20-29, adolescents, etc.) have reported a positive association between PFASs and/or diastolic and systolic blood pressure. Min et al. showed a significant increase in systolic blood pressure as serum levels of PFOA increased among a representative sample of US adults.[45] Bao et al. showed similar results, reporting that this increase in blood pressure was likely caused by oxidative stress brought on by PFAS exposure. These authors also reported that branched isomers of PFASs were more likely responsible for increased blood pressure than their linear counterparts, however branched isomers were not investigated in most other studies on this subject.[46] In adolescent males, Ma et al. showed a positive correlation between PFOS serum concentration and increase in diastolic blood pressure, with no such association existing in adolescent females.[3] Conversely, a positive association between hypertension and increased levels of PFOA in pregnant women was identified during the C8 Science Panel's surveys.[47] As

hypertension is one of the leading causes of death worldwide, the links made between high blood pressure and PFAS serum concentration have serious implications for human health.[46]

Long before any academic studies were performed, 3M and DuPont suspected that PFOA exposure led to potential birth defects, which resulted in the removal of pregnant employees from the Teflon processing line at DuPont.[47] There have been hundreds of studies to date that focus on fetuses accumulating various PFASs in serum via maternal transfer.[48] A majority of review papers on the subject suggest that there is a correlation between maternal PFAS exposure and various birth defects such as decreased birth weight, shorter than average length after birth, and decreased head circumference.[49,50] Unfortunately, the most common PFAS associated with these defects is PFOA, which is also currently one of the most abundant PFASs detected in field samples.[49]

Although the human carcinogenicity of PFASs can only be classified as suspected, animal carcinogenicity has been confirmed via hundreds of studies.[51] Various lifetime studies concerning the effects of PFOA and PFOS on rats have reported a direct link between PFOA-induced activation of PPARα and development and growth of liver tumors.[52] Other tumors in rats (pancreatic, testicular) with a direct link to PFOA exposure have been confirmed, but without a clear mechanism of formation.[41] The C8 Science Panel (formed via a class-action suit against DuPont by Ohio River Valley residents) made links between PFOA exposure and testicular and kidney cancers, which had been previously widely reported in the region (especially among DuPont line

workers).[38] Additionally, the EPA has now classified both PFOA and PFOS as possible carcinogens based on the results of the C8 panel and countless studies since.[53]

Biopersistence and Bioaccumulation

To date, there have been hundreds of studies pertaining to the biopersistence and bioaccumulation of PFASs in the environment.[19,20,54] Multiple PFASs have been found in quantifiable amounts in areas as remote as the arctic tundra.[55] Additionally, as PFASs are soluble in water, they can travel long distances if entering a watershed or ocean current.[54] PFASs are reported to be impervious to natural methods of breakdown such as oxidation and can completely permeate any ecosystems that they enter depending on the extent of the contamination. Bioaccumulation has been observed in multiple types of ecosystems and food chains throughout the world; plants absorb contaminated water through their roots, insects and animals consume contaminated plants and water, and the contamination moves up through the food chain (even exposing humans through contaminated plants and animals).[19,20] Bioaccumulation has been especially prevalent in aquatic animals such as fish, which in turn exposes their natural predators as well as humans.[56,57] The extent of biopersistence and bioaccumulation of PFASs has made them an urgent human and animal health concern.

Remediation

Removal

As PFASs have become more of a public health concern, government regulatory agencies have sought effective methods of removal especially from groundwater and surface water resources. The most popular method of removal to date is the implementation of Granular Activated Carbon (GAC) filters in water treatment systems.[10] PFASs sorb to these filters via ion exchange and are being implemented into wastewater treatment plants. However, the principle behind these filters does not involve destruction, only removal. The removal efficiencies for PFOS and PFOA for an in-use GAC filter are 80% and 60-70%, respectively.[58] However, sorption efficiency can be impacted in multiple ways. Firstly, dissolved organic carbon (DOC) can interfere with sorption of multiple PFASs.[58] Secondly, the sorption of longer-chain PFASs such as PFOA and PFOS can prevent shorter-chain PFASs such as PFBA and PFBS from remaining adsorbed to the carbon.[59] This is especially significant as PFBA and PFBS largely replaced PFOA and PFOS in the mid-2000s; therefore, they are abundant in the environment.[60] Thirdly, time it takes for a filter to be considered spent varies depending on the amount of contamination in the water.[61] Additionally, these filters cannot be used to treat PFAS-contaminated soils. The other two common removal methods, Anion Exchange (AE) resin and membrane nanofiltration, yield similar benefits and drawbacks to GAC filters. In general, AE resin removes PFASs more efficiently via sorption when compared to GAC filters. Again, this method works well for removal, but spent resins

are highly contaminated and need to be disposed of, destroyed, or regenerated with extreme caution.[58] Furthermore, AE resins encounter issues such as sorption interference similarly to GAC (DOC and chain length interference).[58] One of the biggest challenges in using AE resin is selecting the correct material. Polyacrylic resins are more efficient for removing PFOS and PFOA, but polystyrene resins favor shorter chains like PFBA and PFBS. These conditions make selection of a resin for multiple PFASs at various lengths difficult.[62] The most significant drawback regarding membrane filtration stems from the fact that shorter-chain PFASs with smaller molecular weights can often pass through the filter if the pores are too large or made specifically for larger PFASs such as PFOS and PFOA (which are both C8).[63] Overall, these methods still have the same overarching drawback as GAC filters; the PFASs are not destroyed, only removed. An additional step is still needed to completely destroy the PFASs and prevent them from reentering the surrounding ecosystems.

Destruction

As the aforementioned removal methods work best for contaminated water supplies, other methods must be employed to remediate contaminated solids (sediments, plants, manufacturing byproducts). Currently, the most commonly used method of PFAS destruction is incineration at temperatures exceeding 600°C.[10] There are several issues with this method, the first and most important being that several studies have shown that even at extremely high temperatures, incineration is not necessarily completely effective in destroying PFASs if the temperature threshold is not met.[64] Additionally, this method is a source of HF and CO_2 gas production, which are both harmful to human health and

the surrounding environment.[65] This method also involves the complete destruction of the contaminated materials; contaminated solids cannot be remediated for integration back into the environment. Finally, both the environmental and financial costs of incineration are high. Incineration releases a multitude of greenhouse gases into the atmosphere, such as HF and CO_2.[66] Although incineration at the proper temperature (generally exceeding 600ºC) is considered effective,[67] the cost of operating such a system safely is more expensive than other more effective methods of removal and/or destruction.[68]

One of the newer remediation methods for contaminated materials is referred to as plasma-based water treatment (PWT).[10] This method relies on a plasma reactor, which uses the high voltage to generate *in situ* radical species such as aqueous electrons and hydroxyl radicals.[69] Stratton et al. reported that oxidant species (i.e. hydroxyl radicals) do not play a significant role in breakdown of PFOA, and that the most significant contributor to PFOA destruction in plasma was aqueous electrons (e^-_{aq}).[70] As this method can be effectively temperature-controlled and would work well in existing water treatment systems, it is gaining popularity as a means for destroying PFASs such as PFOA.[71] However, Singh et al. reported the generation of byproducts during PFOA and PFOS destruction, including PFHpA, PFHxA, and PFOA (during PFOS breakdown).[71]

Although not yet implemented for PFAS destruction, Electron Beam (eBeam) technology is currently being investigated as an efficient and effective method. eBeam technology employs an accelerator to produce highly energized electrons that are exposed to the target material in a so-called shower of particles. This method has

historically been used for phytosanitation of fresh produce, treatment of imported spices to prevent mold and bacterial growth, sterilization of medical devices, and cross-linking in polymers and electrical wiring.[72] For PFAS destruction, eBeam has the ability to physically breaks the C-F bond which is integral to the molecules' incredible stability. [14] eBeam technology has been shown to effectively break down both PFOS and PFOA at various doses and is currently one of the most promising methods of PFAS destruction.[3,73]

Electron Beam (eBeam) Technology

Technology and Setup

The principle behind eBeam technology lies in the use of highly energized electrons that can cause both direct and indirect damage to DNA and chemicals. This is accomplished via an accelerator, which energizes the electrons to just below the speed of light before they exit through a magnetic scanner.[72] The accelerator itself operates at an energy described in MeV and power measured in kW (Figure 3). Currently, 10 MeV is the highest energy allowed in the US for processing food (higher energies can trigger neutron activation, which would result in transient radiation).[74] However, even at 10 MeV eBeam is classified as ionizing radiation because it is able to remove tightly bound electrons from the target molecule, resulting in those electrons having a negative charge.[14]

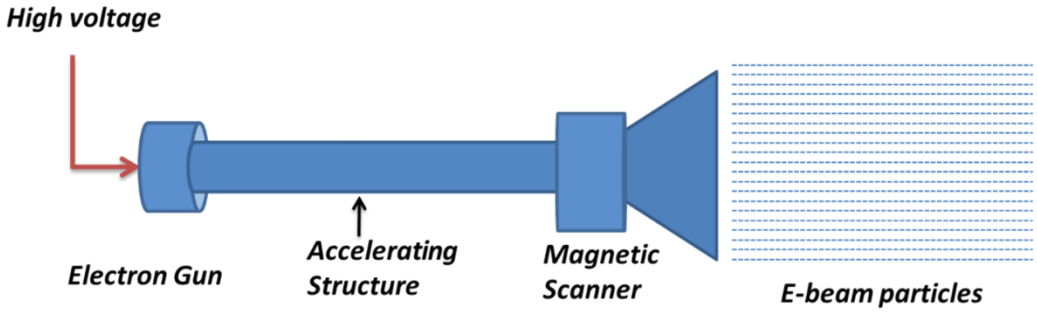


Figure 3. Schematic of Linear Accelerator (LINAC) in eBeam system

There are two mechanisms through which eBeam destroys DNA and chemicals: direct and indirect damage. Direct damage is the result of electrons colliding with atoms and discharging an electron from its orbit. This enables the ejected electron to repeat the process, causing a cascade of reactions in a matter of seconds (Figure 4).[14] Indirect damage is caused when radical species formed by the electrons reacting with water cause oxidative or reductive processes to occur (Equation 1).[75]

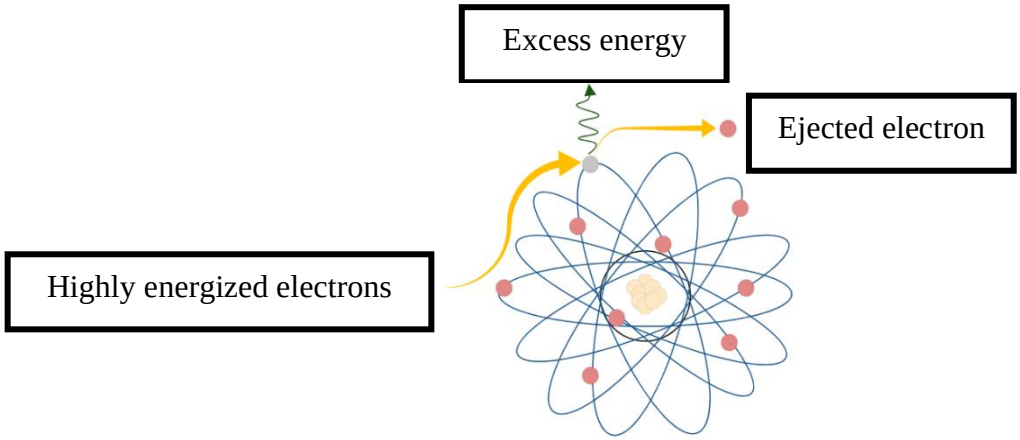


Figure 4. Direct damage caused by highly energized electrons during eBeam irradiation

Both direct and indirect damage are able to cause injury to bacterial DNA (making it an effective process for non-thermal sterilization), break down chemicals originating from

pharmaceutical and industrial waste, and provide phytosanitation to fresh produce.[3,75] One of the emerging uses for eBeam is water and sludge treatment, which uses a pump-and-treat approach, to remediate and reclaim these waste streams for further use.[76] The rising popularity of eBeam technology can be attributed to several factors. Firstly, the only source of energy for accelerators needed for eBeam is conventional electricity. Unlike gamma radiation, the accelerators powering an electron beam can be switched on and off (whereas gamma has a radioactive source that is constantly emitting radiation).[14] However, eBeams do require concrete shielding to protect facility workers while the beam is on. Secondly, eBeam has been widely studied throughout the 20th and 21st centuries, with many uses already identified and put into practice. These applications include (but are not limited to): water remediation, medical device sterilization, irradiation of imported spices, phytosanitation, cross-linking of polymers, and vaccine manufacturing and research.[12,13,72,73] Thirdly, eBeam is widely considered to be much safer and cheaper than similar alternatives. The cost of operating conventional electricity versus radioactive materials is much lower as eBeam does not require the same level of security measures, energy output is constant, and appropriate safety protocols have already been developed for operations (including dose-mapping and irradiation).[14]

Proposed Breakdown Mechanism

The unique reactions that eBeam produces vary from matrix to matrix but have been well quantified in water. Equation (1) shows the radical species produced in water for every 0.1 MeV energy absorbed:

$$0.7H_2O \xrightarrow{Ionizing\ Radiation} [0.27]e^-_{aq} + [0.28]\cdot OH + [0.06]\cdot H + [0.07]H_2O_2 + [0.27]H_3O^+ + [0.05]H_2 \quad (1)$$

As shown in Equation (1), several radical species of both oxidative and reductive natures are produced upon interacting with water. Radical species with high oxidation potential (i.e. hydroxyl radicals) would not cause destruction to a highly oxidized chemical such

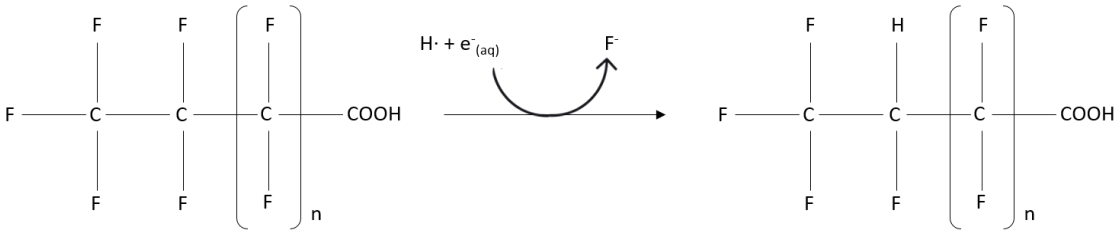


Figure 5. Proposed mechanism for reductive defluorination of PFASs

as PFOA or PFOS.[14] In this particular application, highly reductive species, namely aqueous electrons, are thought to trigger reductive dehalogenation.[26] In this reaction, the covalently bonded fluorine atoms undergo a single-electron exchange with electrons produced during irradiation (Figure 5).

CHAPTER III: EVALUATION OF LOW ELECTRON BEAM DOSES FOR PFOA AND PFOS BREAKDOWN

Introduction

The overall objective of this thesis research was to determine the effectiveness of eBeam in breakdown of PFOA and PFOS, and to determine the conditions and doses that achieve maximum breakdown. We hypothesized that once optimal breakdown conditions were implemented, complete or near-complete destruction of both compounds would be achieved. To accomplish this, we utilized the results of previous studies and determined the starting doses to be 10 kGy and 50 kGy at anoxic and ambient conditions, respectively.[3] These doses were examined with multiple additives ($NaNO_3$, $NaHCO_3$, NaOH, and N_2 sparging) as well as lab-spiked and field samples, and analyzed using LC-MS/MS.

The low-dose portion of this research provided valuable insight into the minimum dose required to completely break down PFOA (50 kGy) and established that breakdown of PFOS would require much higher doses and possibly adjustment of the sample conditions.

Materials and Methods

Reagents and preparation of stock solutions

Analytical grade reagents including Powdered PFOS-K (Perfluorooctane Sulfonate Potassium Salt) and Powdered PFOA (Perfluorooctanoic Acid) were obtained from Sigma Aldrich (St. Louis, MO) were also obtained from Sigma Aldrich (St. Louis, MO). PFASs dissolved in Methanol for preparation of stock solutions or for use as analytical standards were purchased from Wellington Labs (Guelph, Ontario).

Experimental vessels

High-Density Polyethylene bottles for sample preparation and storage and polypropylene bags for transfer were purchased from VWR (Radnor, PA). Alanine dosimeters used for dose mapping and dose absorbed were purchased from Bruker Scientific LLC (Billerica, MA).

Electron Beam Treatment

The eBeam trials were performed at the National Center for Electron Beam Research (NCEBR), which is located on-campus at Texas A&M University, College Station, TX. This facility is used for both research and commercial projects, and employs two 10 MeV, 18 kW Electron Beam Linear Accelerators (LINAC). The dose each sample received was previously determined through the use of dose-mapping and calculating the speed in feet per minute that the conveyor belt must run at to achieve the desired dose. This was achieved by affixing dosimeters beneath, within, and atop sample bottles containing 10g sand, 50g sand, 10 mL water, and 50 mL water. Each dose was

read and used to calculate the dose uniformity ratio (DUR) of each sample. The two samples with the DUR closest to one were 10g sand and 50 mL water, so these samples were determined to be the best for the eBeam experiments. Dose received was confirmed via alanine dosimeters handled by the NCEBR staff dosimetrist.

Sample Preparation

To prepare the lab-spiked samples, stock and working solutions were made in the chemical fume hood. The determined concentrations were different for each desired chemical in each matrix: 5 µg/L PFOA and 10 µg/L PFOS in each water sample, and 10 mg/kg PFOA and 20 mg/kg PFOS in each sand sample. Each stock was prepared separately for water and sand samples, as the concentrations needed for the sand samples were not sold in aqueous form. To prepare the stock solution for the water samples, a 10x dilution in 100% MeOH was made from the pure chemical dissolved in MeOH. The stock was then further diluted into a working solution made with HPLC-grade water to achieve the desired concentration. PFOA and PFOS were combined into one working solution from their respective stocks; the working solution had final concentrations of 5 µg/L PFOA and 10 µg/L PFOS. 50 mL of working solution was dispensed into 60 mL square HDPE bottles for irradiation.

The working solution for the sand samples was prepared using pure powdered PFOS-K and PFOA. Both powders were first dissolved in acetone before being added to a 1 L volumetric flask. After the entirety of the pure powder solution was rinsed into the flask, the remainder was filled to the 1 L line with HPLC-grade water. The final concentration of the working solution was 10 mg/L PFOA and 20 mg/L PFOS. 10 mL of

the working solution was added to 10 g of sand to achieve the final concentrations of PFOS and PFOA. Sand and water samples were pH-adjusted with 10 N NaOH to achieve pH 13. All samples also included the following additives: 0.1M Sodium Nitrate ($NaNO_3$) and 1M Sodium Bicarbonate ($NaHCO_3$) to improve the production of aqueous electrons during eBeam treatment. Some samples were also sparged and flooded with pure nitrogen gas to create a low-oxygen environment.

Field samples were collected from Randolph Air Force Base in San Antonio, TX and the Texas A&M University wastewater treatment plant in College Station, TX. All field samples were stored at 10^{o}C in HDPE bottles and preparation was performed in the same manner as lab-spiked samples (in a chemical fume hood with proper PPE).

eBeam Treatment

To determine the speed of the belt on which the samples passed through the beam, the DUR (Dose Uniformity Ratio) was first calculated. This involved affixing alanine dosimeters on top of, within, and beneath each sample, recording the dose received, and calculating the ratio of the maximum vs. the minimum dose (desired DUR is 1.0). 50 mL and 10 mL of water as well as 10 g and 50 g of sand were tested to determine which amount of sample for each matrix achieved the most uniform dose. Based on these tests, the samples selected for testing were 50 mL of water and 10 g of sand. Two doses of irradiation were initially selected for testing: 10 kGy and 50 kGy. Further in the experiment, samples were subjected to the following doses: 50 kGy, 100 kGy, 250 kGy, and 500 kGy (only water samples were tested at these doses). To achieve these doses, samples were irradiated at the appropriate belt speed and passed through the

beam several times, building dose with each pass. After treatment, all samples (control and eBeam) were stored at 10^{o}C until analysis.

Post-eBeam treatment sample processing

To ensure that the presence of extraneous organic compounds did not interfere with the downstream LC-MS/MS analyses, the experimental samples were purified and concentrated using SPE (solid phase extraction) columns (Waters Oasis WAX). The water samples, being relatively a relatively straightforward matrix, could be extracted immediately after irradiation. The sand samples, which were a mixed solid/liquid matrix, had to go through an additional extraction step pre-SPE. This extraction involved adding 25 mL 0.1% ammonium hydroxide in methanol to each sample and sonicating (Branson Model 1800 CPHX series) for one hour. After sonication, the supernatant was poured into a new bottle and the process was repeated, combining the supernatants after the final sonication. The supernatant was then sonicated for an additional 30 minutes, after which 1.5 mL of solution was pipetted into a 2 mL centrifuge tube. These samples were then further purified using the …From there, each sample was extracted using SPE.

The SPE process involved 1 mL Oasis WAX cartridges purchased from Waters (Milford, MA) in a vacuum manifold setup that were conditioned with 0.1% Ammonium Hydroxide in Methanol three times followed by 100% Methanol three times. After the last of the 100% Methanol was through the cartridge filter, 1 mL of each sample was loaded into the cartridges and low vacuum was used if necessary. After sample loading, each cartridge was washed with 1 mL 25 mM Ammonium Acetate, then dried for 3-5 minutes with vacuum. After each cartridge was sufficiently dried, elution with 1 mL

0.1% Ammonium Hydroxide in Methanol was completed with vacuum. The elution was collected in a separate vial and immediately covered with Parafilm before being transferred to 250 µL vials for LC-MS/MS analysis.

LC-MS/MS Analysis

PFOS and PFOA were identified and quantified on a triple quadrupole mass spectrometer (Altis, Thermo Scientific, Waltham, MA) attached to a binary pump HPLC (Vanquish, Thermo Scientific). To provide the most optimal MS conditions, selective reaction monitoring (SRM) transitions were identified at a direct infusion rate of 5 µL/min. The SRM transition values for PFOS and PFOA are included in Table 1.

Compound	**Polarity**	**Precursor (m/z)**	**Product (m/z)**	**Collision Energy (V)**	**RF Lens (V)**
PFOS	Negative	499.000	79.917	34.87	137
PFOA	Negative	413.000	368.988	10.23	42

Table 1. Quantitative SRM Transitions for compounds

SRM (selected reaction monitoring) describes the precursor and product ions formed during the two fragmentation stages of LC-MS/MS. This process allows for the operator to select fragments (described as m/z, or mass/charge) that will result in the least amount of "noise", and therefore provide results that are easier to interpret. [77] The injection volume was 10 µL. Chromatographic separation was achieved on a Hypersil Gold 5 µm 50 x 3 mm column (Thermo Scientific) maintained at 30 °C using an 8-minute solvent gradient method. The flow rate was 0.5 mL/min, with sample

acquisition performed by TraceFinder 3.3 (Thermo Scientific). Analysis results were reported as concentration of desired PFAS in ng/mL.

Results

Lab-Spiked Samples

Both lab-spiked water and saturated sand samples showed destruction of PFOA post-eBeam treatment at 50 kGy or higher. No decrease was seen at 10 kGy in any samples. Although there was an 87.6% breakdown of PFOA at 50 kGy in lab-spiked water (Figure 6), the percent breakdown in PFOS in the same samples was only 16.1% (Figure 6). The saturated sand samples showed similar breakdown patterns; the concentration of PFOA decreased by 86.3% (Figure 7), with the concentration of PFOS decreasing by 27.6% (Figure 7).

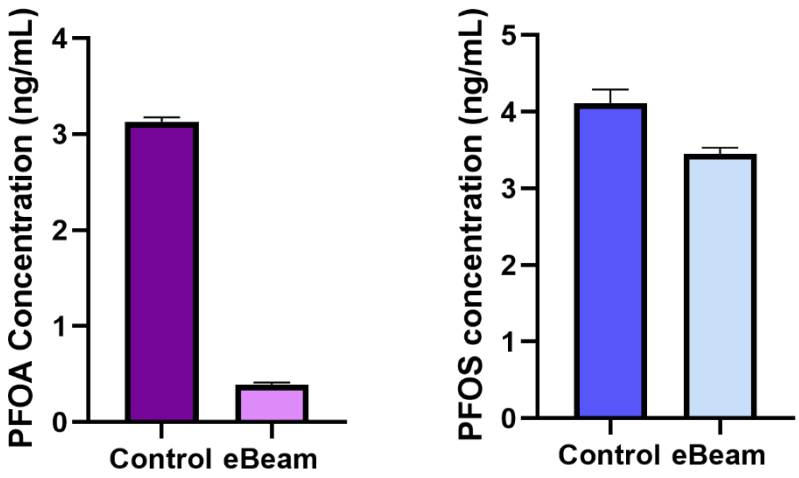


Figure 6. Breakdown of PFOA (left) and PFOS (right) in lab-spiked water at 50 kGy

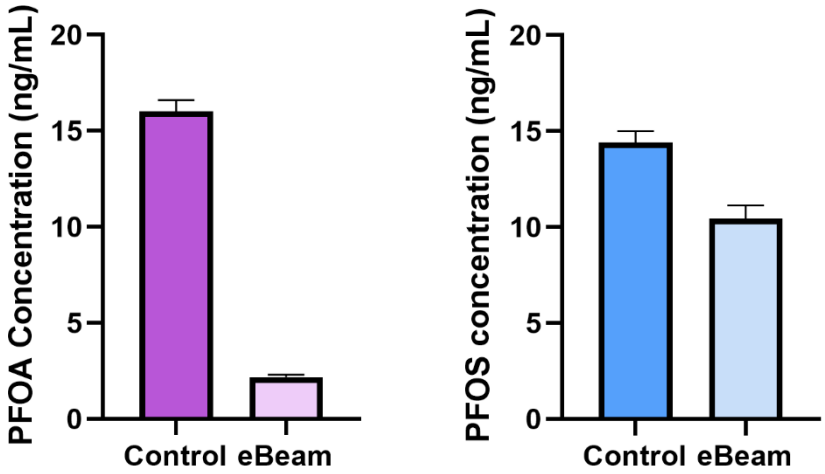


Figure 7. Breakdown of PFOA (left) and PFOS (right) in lab-spiked sand at 50 kGy

As shown in Figure 8, the breakdown of PFOS did not increase until the dose reached 500 kGy (Table 2).

Dose	Percent PFOS Reduction
50 kGy	34.85
100 kGy	28.08
250 kGy	29
500 kGy	40.05

Table 2. Percent PFOS reduction in lab-spiked water samples at various doses

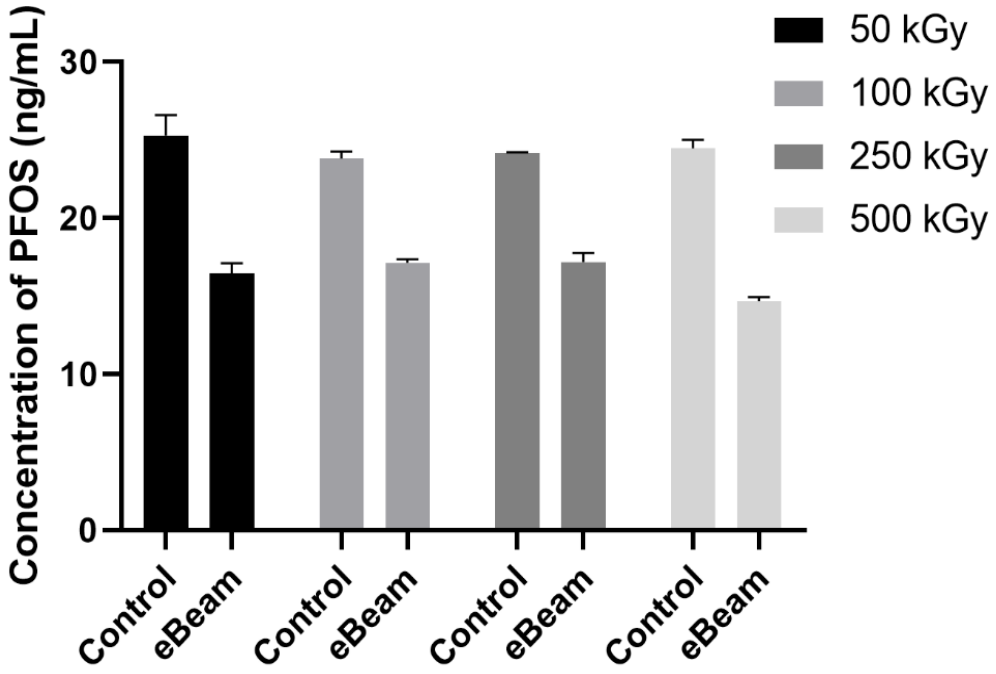


Figure 8. Breakdown of PFOS in lab-spiked water at various doses

The percent breakdown at 100 and 250 kGy was nearly the same, whereas the 50 kGy result was closer to the 500 kGy result (Table 2).

Field Samples

Two groups of field samples were irradiated at 50 kGy after being spiked with PFOS (10 μg/L) and PFOA (5 μg/L): Post-UV wastewater effluent from the Texas A&M Wastewater treatment plant in College Station, TX; and Groundwater collected from a

monitoring well onsite at Randolph Air Force Base in San Antonio, TX. Each set of control and eBeam samples were analyzed using a larger set of analytical standards, and the detected compounds are shown in Figures 9 and 10 below.

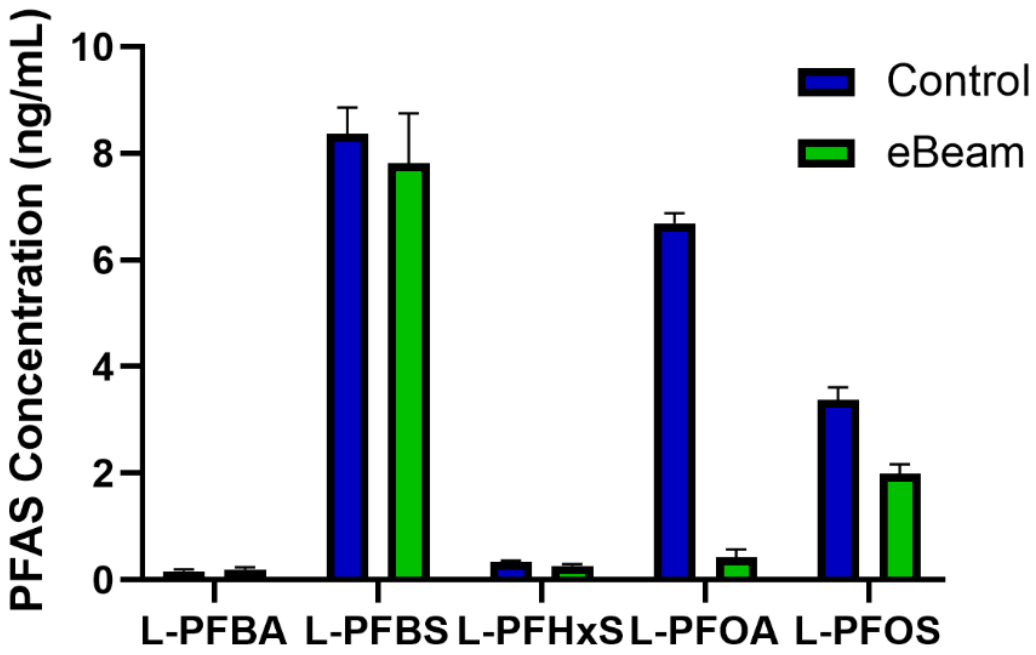


Figure 9. Fate of various PFASs in lab-spiked wastewater effluent at 50 kGy

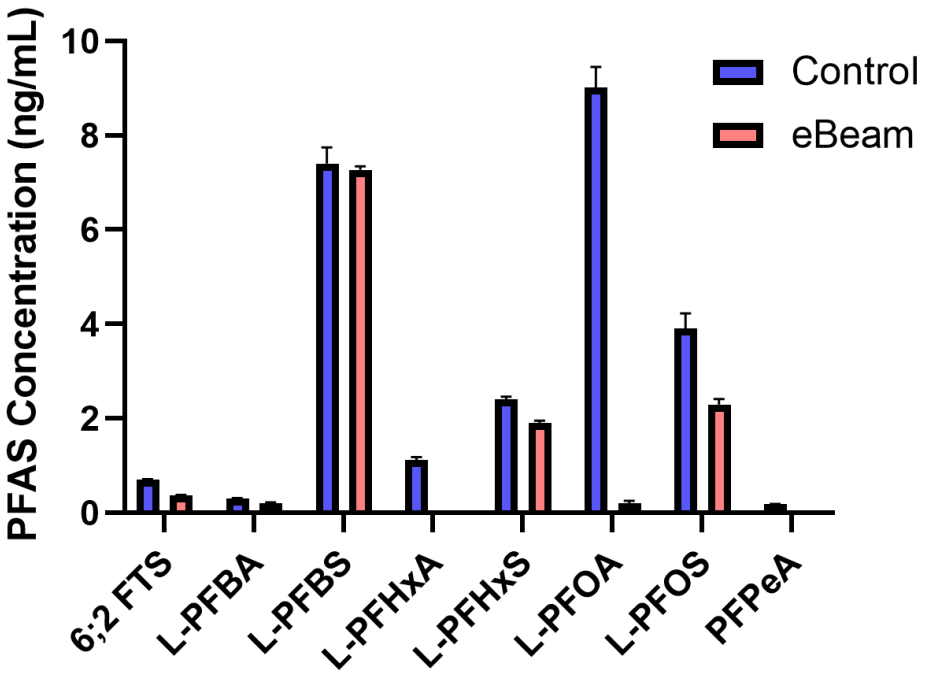


Figure 10. Fate of various PFASs in lab-spiked groundwater at 50 kGy

Table 3 describes the breakdown (or increase) of each detected PFAS in wastewater effluent and groundwater samples.

	Wastewater Effluent	Groundwater
6;2 FTS	N/A	47.81
L-PFBA	Increase by 19.47	32.29
L-PFBS	6.66	1.84
L-PFHxA	N/A	100
L-PFHxS	21.93	20.54
L-PFOA	93.65	97.79
L-PFOS	41.19	41.06
PFPeA	N/A	100

Table 3. Percent breakdown of various PFASs in wastewater effluent and groundwater samples

Discussion

The aim of this study was to discover whether or not PFOA and PFOS can be broken down using eBeam technology. If so, researchers further desired to determine the amount of breakdown and the dose necessary to achieve it. Furthermore, the overarching goal of this research was to achieve complete or near-complete breakdown of PFOA and PFOS. Multiple samples analyzed post-eBeam treatment showed near-complete breakdown of PFOA at doses of 50 kGy or higher, and 16-40% breakdown of PFOS depending on the dose and sample matrix. Although the attempts to break down PFOA were highly successful, we determined that a higher dose (possibly combined with other treatments) would be necessary to achieve the same success with PFOS. Compared to

existing methods of removal or breakdown, the results of this study showed that eBeam has potential in becoming an *in situ* treatment for both water and soil.

Traditionally, the most common method of PFAS destruction was incineration at temperatures exceeding 600^{o}C.[10] This method, which is both costly and involves the complete loss of affected materials (soil, water, sludge) has been on the decline in terms of popularity in favor of sorption methods or more cost-effective breakdown methods.[78] The current method with the most use in situ is the implementation of granular activated carbon, or GAC, filters in water treatment facilities. When compared to GAC and other alternative removal processes (such as anion exchange resin), eBeam continued to outperform every method in terms of success rate (i.e. removal efficiency of GAC vs. percent breakdown of PFOA via eBeam).[62,79,80] As previously mentioned, another highly successful treatment has been found in plasma-based systems, but to our knowledge is not yet widely used by water treatment facilities.[71,81]

Granular activated carbon is a widely used sorption method for chemical contaminants such as PFASs in water treatment plants. However, unlike eBeam treatment, which can break down PFASs, GAC is only effective for removal. Additionally, spent GAC is heavily contaminated and must still be disposed of via incineration or a similarly effective method8. Compared to eBeam treatment, which saw 97.79% breakdown of PFOA in groundwater and 93.65% breakdown in wastewater effluent, GAC's ability to sorb PFASs can vary based on presence of organic matter, type of PFAS, carbon fouling, and pre-washing of the filters (however, there is some disagreement in literature on how well GAC removes PFASs; some studies show >90%

removal efficiency).[63,82] Similarly to GAC, anion exchange (AE) resins do not function uniformly throughout all matrices or for all PFASs; certain anionic compounds can interfere with the removal process.[62] More experimentation will be necessary to determine the most effective way to break down all PFASs in water using eBeam technology, however, lack of interference from organic matter in the wastewater effluent and groundwater in this study demonstrated by the successful breakdown of PFOA showed the potential of eBeam in water remediation applications.

The choice to include additives such as sodium carbonate and sodium nitrate was motivated by previous literature that showed a linear relationship between defluorination efficiency and carbonate/nitrate concentration.[3] Similarly, the decision to increase the pH of each sample to 13 stemmed from literature that showed that the degradation rate of PFOA increased twenty-fold after increasing the pH from 7 to 13.[9] These additives proved to be effective for breakdown of PFOA, but the increased breakdown of PFOS was mediated by increased dose (Figure 8).

Based on the results of this study, breakdown of PFOS increased with dose received. This is reflected in literature (although few publications currently exist); a previous study employed doses of up to 2000 kGy to achieve complete or near-complete breakdown of PFOS.[83] Another study produced similar results and further postulated that aqueous electrons were the major route of degradation in water samples without additives, and these samples produced the highest amount of PFOS degradation.[73] These findings further strengthen the notion that the dominant factor in eBeam-mediated breakdown of PFOS is not additional additives, but additional dose.

As mentioned previously, the aqueous electrons produced during eBeam treatment are strong reductive agents; PFASs undergo a single-electron exchange with aqueous electrons that results in defluorination of the PFAS.[14] Based on this concept and the complete breakdown of PFOA in all water samples treated at 50 kGy or higher, eBeam treatment has proven to be an effective method for breaking down PFOA in water.

Presently, few methods of remediation and/or disposal exist for PFAS-contaminated soils. Most publications investigate the chemical interactions of PFASs with soil and groundwater, which are critical to forming a robust method for remediation. Prior studies have demonstrated that PFASs with C-F chains of 11 molecules or longer predominantly sorb to soil particles,[84] with shorter chains favoring water molecules in the pores of the soil.[85] With the focus of this study being on PFOA and PFOS (both eight-Carbon chains), one study of particular interest demonstrated that PFOS had a higher affinity for soil particles than PFOA.[18] It is unclear how these characteristics contribute to the breakdown of PFOA or PFOS, since the results of the saturated sand samples mirrored those of the water samples. Although no soil experiments were included in this chapter, from previous literature and results, there is reason to believe that soil samples with a higher moisture content would further mediate the breakdown of these chemicals, especially PFOA. For this reason, (and for ease of extraction), sand samples were completely saturated with water to encourage the formation of aqueous electrons responsible for defluorination.

As previously stated, incineration of affected materials is on the decline due to inefficiency and cost. The EPA states that one of the most promising methods of remediating PFAS-contaminated soil is soil sorption technology, which immobilize PFASs in soil before they are able to contaminate surrounding groundwater.[86] After sorption, remediation would still involve either a pump-and-treat approach, or spent sorption materials would need to be incinerated.

There is currently a lack of diverse publications on destruction of PFASs in soil for remediation purposes. However, the results of this study were promising; 86.3% breakdown of PFOA and 27.6% breakdown of PFOS were achieved in lab-spiked saturated sand samples. As these samples were only meant to simulate soil samples, more research is needed to determine the success rate of eBeam in destroying PFASs in soils. However, as all of the previously mentioned studies were performed on water and not soil samples, the results of this study are currently the most promising data available that investigates the possibility of remediation of contaminated soil via destruction and not adsorption.

There are several experiments not included in the low dose studies that still hold significance for *in situ* remediation using eBeam technology. The first and most important experiments would study the breakdown products, if any, of PFOA and PFOS after they have been broken down using eBeam. Theoretically, relying on the principle of reductive dehalogenation, shorter chains could form after parts of the fluorocarbon chain have been broken down. Shorter chain PFASs such as PFBS (a four-Carbon PFAS) have still been shown to have negative effects in humans.[40] The other

experiments, which will be further discussed in Chapter IV, are those involving soil field samples. These studies would also provide valuable data for possible *in situ* application of eBeam, especially as soil varies so extensively from region to region. Additionally, characterizing PFAS breakdown in solid matrices is of utmost importance due to their ability to sorb to soil particles.

Conclusions

The experiments performed in this study showed near-complete breakdown of PFOA, but insufficient breakdown of PFOS. The original hypothesis stated that at optimal conditions, PFOA and PFOS would experience complete or near-complete breakdown. This was achieved for PFOA, but more studies are needed to determine the optimal conditions for PFOS breakdown. Experiments studying the efficacy of eBeam in organic solid matrices such as soil are also necessary in order to determine the applicability of eBeam for contaminated solids remediation.

CHAPTER IV: EVALUATION OF HIGH ELECTRON BEAM DOSES FOR BREAKDOWN OF PFOS

Introduction

PFOS is one of the most studied and most prevalent PFASs found in nature and human serum.[1,2] The lack of complete breakdown of PFOS in samples in Chapter III indicated a need for further experiments using higher eBeam doses. Previous literature provided evidence that extremely high doses (exceeding 500 kGy) are effective in completely breaking down PFOS.[83] Using a stainless steel and aluminum boat crafted by collaborators in the Department of Mechanical Engineering at Texas A&M, high doses with correspondingly high temperatures were applied to lab-spiked water and field soil samples.

As discussed in Chapter III, a dose as high as 500 kGy does not necessarily ensure complete breakdown of PFOS. However, the 500 kGy samples were treated by building dose in batches (several passes underneath the beam after which cumulative dose reached 500 kGy). For the high dose experiments in this chapter, sample containers for the experiments in this chapter were designed to allow doses as high as 2000 kGy to be applied in one continuous dose of irradiation. The new containers specifically accounted for the high-pressure environment created within the sample container during irradiation. The amount of energy deposited during this process also caused temperatures

within the sample containers to reach 100°C, which we believe aided in the breakdown of PFOS.[67,87]

We first performed experiments using lab-spiked water and sand samples, which were made using working solutions prepared with pure concentrates of PFOA and PFOS. Field samples were obtained from a PFAS-contaminated lake in Michigan, USA for irradiation at high doses. The underlying hypothesis of this study was that high doses of eBeam irradiation, when delivered in one continuous dose, would be capable of completely breaking down PFOS and PFOA in water and soil samples.

Materials and Methods

Chemicals, Reagents, and Consumables

All reagents were purchased from Sigma Aldrich (St. Louis, MO) and were of analytical grade. PFASs dissolved in Methanol for preparation of stock solutions or for use as analytical standards were purchased from Wellington Labs (Guelph, Ontario). High-Density Polyethylene bottles for sample preparation and storage and polypropylene bags for transfer were purchased from VWR (Radnor, PA). Alanine dosimeters used for dose mapping and reading absorbed dose were purchased from Bruker Scientific LLC (Billerica, MA).

Preparation of Samples

Lab-spiked samples were prepared using working solutions made with the PFOA and PFOS concentrates purchased from Sigma Aldrich and Wellington Labs. Water

samples were made by diluting the PFOA/PFOS to the desired concentration; sand samples were spiked with water at the desired concentration of PFOA/PFOS, with the volume of water added being equal to the mass of the sand (20 g sand spiked with 20 mL water). Field samples were retrieved by AECOM; surficial soil samples were gathered from a PFAS-impacted lake in Michigan. The amended samples were spiked and pH-adjusted prior to being dried down to 10% moisture in a laboratory oven overnight at 75^{o}C (Fischer Scientific IsoTemp 500 Series). Amendments ($NaHCO_3$, $NaNO_3$, and 10N NAOH) were prepared at 1M, 0.1M, and 10N respectively. Selection of amendments was based on results in Chapter III. Predetermined amounts of each were dispensed into each sample to achieve the desired concentration of each amendment.

eBeam Facility

All eBeam experiments were performed at the National Center for Electron Beam Research (NCEBR), which is located on-campus at Texas A&M University, College Station, TX. This facility is used for both research and commercial projects, and employs two 10 MeV, 18 kW Electron Beam Linear Accelerators (LINAC). The dose each sample received was previously determined through irradiating a sample with alanine dosimeters attached for 10-15 seconds. The measured dose received (in kGy) from these dosimeters determine the appropriate time needed for the beam to contact the samples in order to deliver the desired dose (500 or 2000 kGy). All dosimeters were handled and read by the NCEBR staff dosimetrist.

eBeam Irradiation

For high dose irradiations, doses were delivered in one continuous session rather than making multiple passes underneath the beam on the conveyor belt. For these samples, a special setup was created by collaborators in the Department of Mechanical Engineering at Texas A&M to allow samples to stay underneath the beam without causing damage to their container (Figure 11).

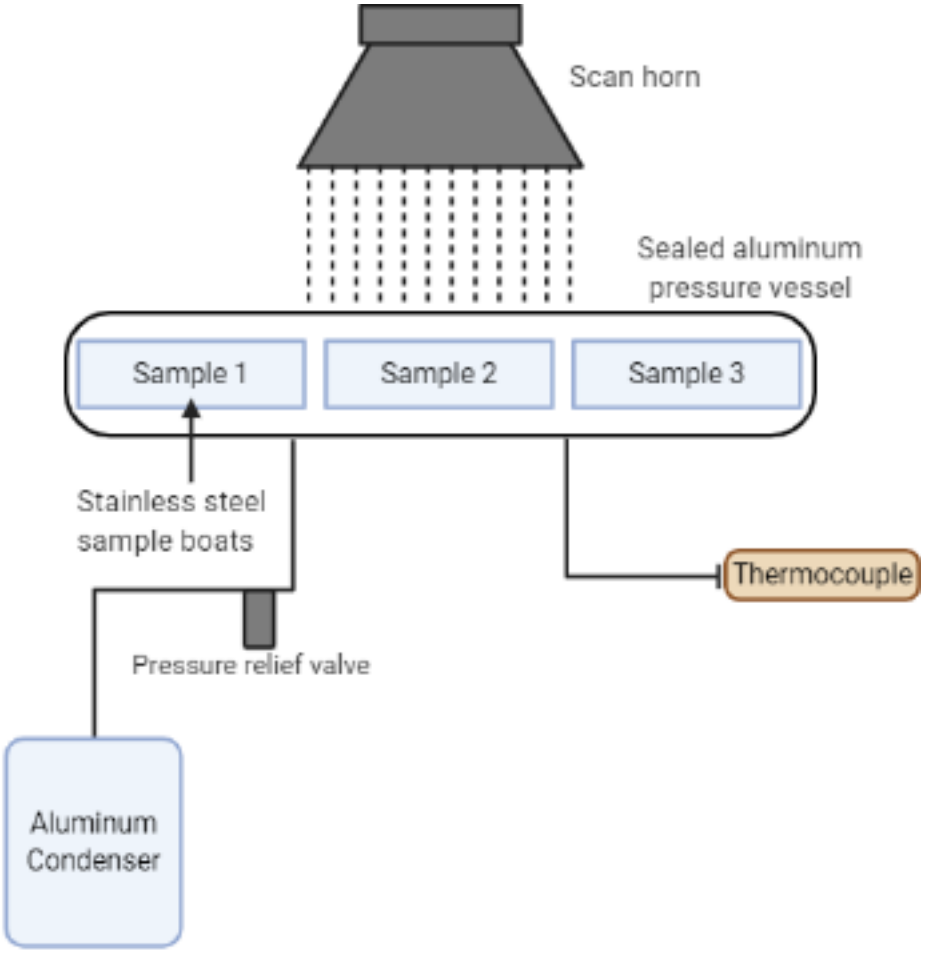


Figure 11. High-dose eBeam container schematic

Samples (soil, water, or saturated sand) were placed inside stainless steel boats, which were in turn placed inside the sealed pressure vessel. Piping connected the vessel to a secondary aluminum container, which allowed any evaporated water to condense and be collected for analysis (Figure 12). Samples were irradiated at either 500 kGy or 2000 kGy. Between each sample group and at the end of each day, all pipes and containers in this setup were flushed with 100% methanol, sanded down, and flushed with methanol a second time. This prevented cross-contamination between samples.

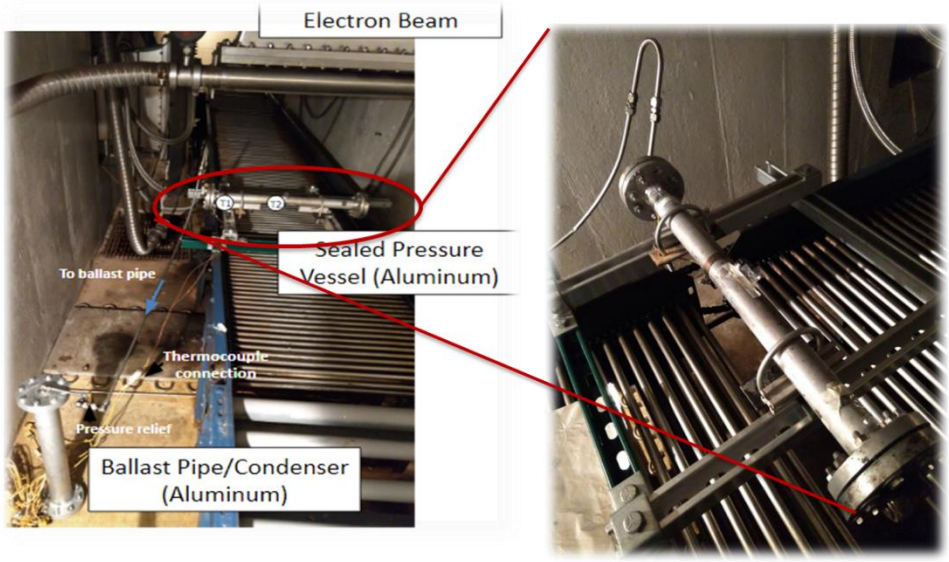


Figure 12. Photographs of high-dose container configuration

Pre-Analysis Extraction

To ensure that the presence of any organic compounds did not interfere with the LC-MS/MS analysis, both sand and water samples were extracted using SPE (solid phase extraction). The water samples, being a relatively straightforward matrix, could be extracted immediately after irradiation. The sand samples, which were a mixed

solid/liquid matrix, had to go through an additional extraction step pre-SPE. This extraction involved adding 25 mL of 0.1% ammonium hydroxide in methanol to each sample and sonicating for one hour (Branson Model 1800 CPHX series). After sonication, the supernatant was poured into a new bottle and the process was repeated, combining the supernatants after the final sonication. The supernatant was then sonicated for an additional 30 minutes, after which 1.5 mL of solution was pipetted into a 2 mL centrifuge tube. From there, each sample was extracted using SPE.

The SPE process involved 1 mL Oasis WAX cartridges purchased from Waters (Milford, MA) in a vacuum manifold setup that were conditioned with 0.1% ammonium hydroxide in methanol three times followed by 100% methanol three times. After the last of the 100% methanol was through the cartridge filter, 1 mL of each sample was loaded into the cartridges and low vacuum was used if necessary. After sample loading, each cartridge was washed with 1 mL of 25 mM ammonium acetate, then dried for 3-5 minutes with vacuum. After each cartridge was completely dried, elution with 1 mL of 0.1% ammonium hydroxide in methanol was completed with low vacuum. The elution was collected in a separate vial and immediately covered with Parafilm before being transferred to 250 µL vials for LC-MS/MS analysis.

LC-MS/MS Analysis

PFOS and PFOA were identified and quantified on a triple quadrupole mass spectrometer (Altis, Thermo Scientific, Waltham, MA) attached to a binary pump HPLC (Vanquish, Thermo Scientific). To provide the most optimal MS conditions, selective

reaction monitoring (SRM) transitions were identified at a direct infusion rate of 5 µL/min. The SRM transition values for PFOS and PFOA are included in Table 1.

Compound	**Polarity**	**Precursor (m/z)**	**Product (m/z)**	**Collision Energy (V)**	**RF Lens (V)**
PFOS	Negative	499.000	79.917	34.87	137
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Table 4. Quantitative SRM Transitions for compounds

SRM describes the precursor and product ions formed during the two fragmentation stages of LC-MS/MS. This process allows for the operator to select fragments (described as m/z, or mass/charge) that will result in the least amount of "noise", and therefore provide results that are easier to interpret. [77]

The injection volume was 10 µL. Chromatographic separation was achieved on a Hypersil Gold 5 µm 50 x 3 mm column (Thermo Scientific) maintained at 30 °C using an 8-minute solvent gradient method. The flow rate was 0.5 mL/min, with sample acquisition performed by TraceFinder 3.3 (Thermo Scientific). Analysis results were reported as concentration of desired PFAS in ng/mL.

Results

Figure 14 shows the reduction of PFOS in lab-spiked water samples at doses of 500 kGy and 2000 kGy, with and without amendments. At 500 kGy, the mass of PFOS in the unamended sample decreased by 21.8%, and at 2000 kGy the mass in the unamended sample decreased by 96.6%. At 2000 kGy, the amended sample only experienced 88.8% breakdown; approximately 8% less than that of the unamended sample.

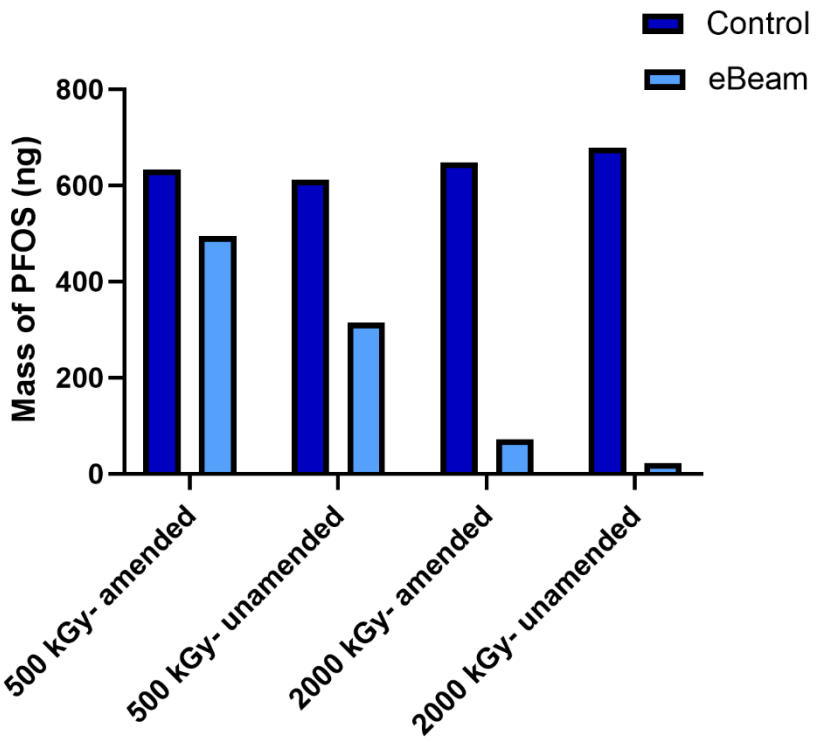

Figure 13. Destruction of PFASs in lab-spiked water at 500 and 2000 kGy

The sand samples showed 97-100% PFOS destruction at all doses, and both with and without amendments (Table 5). Both samples treated at 2000 kGy collected from the stainless-steel boats showed that PFOS had been degraded to below the detection limits of the LC-MS/MS (detection limit is 0.025 ng/g).

Sample Group	Sample	PFOS in sample (µg)	% Reduction
500 kGy- amended	Control	189.7	____
	eBeam	2.27	98.80
	Condensate	2.20	98.84
2000 kGy- amended	Control	201.25	____
	eBeam	0.02	~100
	Condensate	5.16	97.44
2000 kGy- unamended	Control	197.15	____
	eBeam	0	100
	Condensate	2.75	98.60

Table 5. Destruction of PFOS at 500 and 2000 kGy with and without amendments

The IDW samples gathered in Michigan were analyzed using a longer list of analytes in order to provide the background levels of all PFASs present in the samples and/or identify breakdown products. Table 6 shows that the 10% moisture-adjusted

samples experienced an average of 96.6% breakdown across all detectable compounds. PFBS showed the least amount of breakdown in this sample group at 72.65% destruction. Nine of the fifteen compounds were undetectable post-irradiation. Unamended samples saw an average of 93% reduction in all detectable compounds. PFOS saw the least amount of degradation in this sample group at 76.99%. Seven out of fifteen compounds were destroyed below detection limit in the unamended sample group.

PFAS Analyte	Control (µg)	Unamended Samples		10% Moisture-Adjusted Samples	
		Mass (µg)	% Reduction	Mass (µg)	% Reduction
4:2 FTS	0.288	0	100	0	100
6:2 FTS	3.66	0.25	93.17	0	100
8:2 FTS	3.72	0.567	84.78	0	100
L-PFBA	1.63	0.132	91.89	0.23	85.88
L-PFBS	1.14	0.132	88.43	0.312	72.65
L-PFHxA	3.01	0	100	0	100
L-PFHxS	5.45	0.845	84.53	0	100
L-PFOA	2.81	0.22	92.19	0.232	91.74
L-PFOS	39.7	9.13	76.99	0.0376	99.91
PFDA	0.0486	0	100	0	100
PFHpA	2.31	0	100	0.0095	99.59
PFHpS	0.223	0.0363	83.7	0	100
PFNA	0.312	0	100	0	100
PFPeA	9.68	0	100	0.0238	99.75
PFPeS	2.11	0	100	0	100

Table 6. Destruction of PFASs in IDW soil at 2000 kGy

Figure 15 highlights the breakdown of PFOA and PFOS in the unamended and 10% moisture-adjusted sample groups. When an independent student t-test was performed on each sample group compared to control (95% confidence interval), all sample groups were found to be significantly different from their respective control groups ($p < 0.05$). However, the unamended and 10% moisture-adjusted samples were not significantly different from each other when examining the destruction of both PFOA and PFOS ($p > 0.05$).

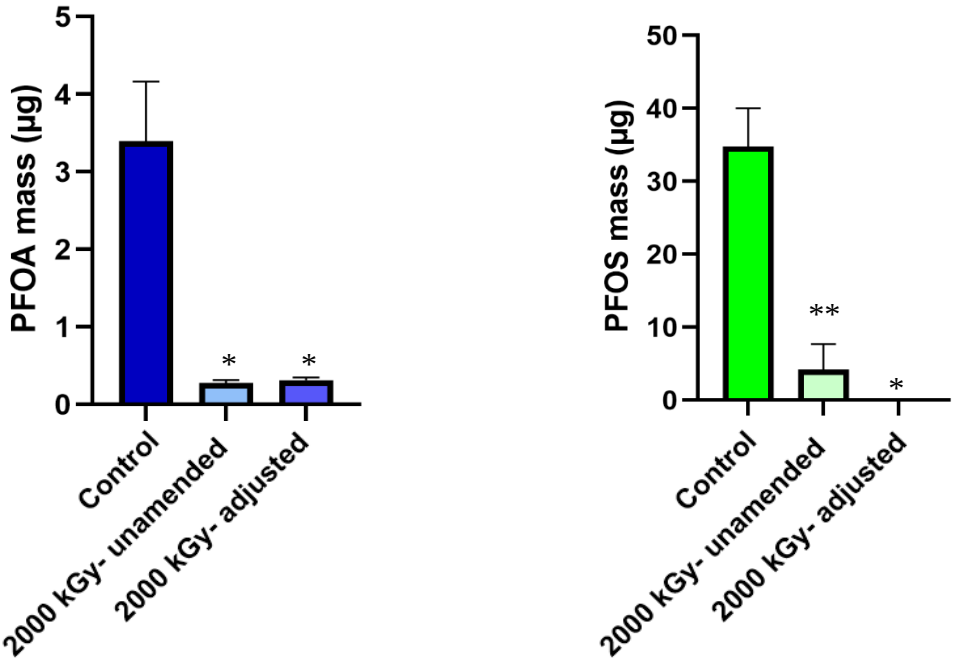

Figure 14. Breakdown of PFOA and PFOS at 2000 kGy with and without amendments (* and ** indicate $p<0.05$ and $p<0.01$ at 95% confidence interval)

Discussion

The results of the lab-spiked water and sand show that at 2000 kGy, eBeam technology is capable of completely breaking down PFOS. Interestingly, the unamended samples experienced more degradation of PFOS than the amended samples. However, Trojanowicz et al. recently showed that at concentrations as low as 10 ng/mL, the presence of nitrate can inhibit the desulfonation of PFOS during eBeam irradiation.[88] This is significant because the sulfonate functional group is a major contributing factor to the versatility and strength of the PFOS molecule in water.[89] Based on these results, the nitrate and carbonate amendments were not included in subsequent experiments. As previously mentioned, we also postulated that high temperatures reached during high-dose irradiation would help mediate further breakdown of PFOS. The results of the thermocouple data from the lab-spiked sand experiments showed that the maximum temperatures reached at each dose (100^{o}C for 500 kGy and 520^{o}C for 2000 kGy), and that the temperature remained higher for much longer for the 2000 kGy samples. Temperatures began to decline to below boiling at approximately 90 seconds during the 500 kGy run, whereas temperatures remained above 300^{o}C even after 6.5 minutes during the 2000 kGy run.

The complete breakdown of PFOS in lab-spiked sand samples at 2000 kGy (Figure 15) led us to hypothesize that the same dose would be equally as effective in IDW (investigation-derived waste) soil samples. The amendments for the 10% moisture-adjusted samples still included adjustment to pH 13 using NaOH, as previous literature

showed a direct relationship between PFOS breakdown and increasing pH.[83] Additionally, sulfonates are known to be stable at mildly acidic conditions.[90] This is especially relevant as pH readings taken of pure water samples spiked with PFOS showed the average pH to be 5.25 (Appendix B). Although the unamended sample group and the 10% moisture-adjusted sample group were not shown to be significantly different from each other, the latter was the only group to show complete breakdown of PFOS (Figures 14 and 15). These results suggest that at high doses, eBeam technology is most efficient for PFOS breakdown at low moisture content and high pH.

The results of the IDW soil sample irradiation also show that at 2000 kGy, all other detectable PFASs experienced significant reduction (Table 4). All fluorotelomer precursors (FTS) were completely broken down. These precursors are raw materials used during the manufacturing of PFASs and can degrade into various PFASs such as PFOA.[91] All of the longest-chain PFASs included in the analysis (PFNA, PFPeA, and PFPeS), all of which had 9 or more carbon atoms in their fluorocarbon chain, were also completely degraded. We hypothesized that some of the shorter-chain PFASs might be breakdown products of PFOA and PFOS, and although this was not conclusively proven through our experiments, the breakdown of PFBA and PFBS in both sample groups still shows the effectiveness of the technology. These results are noteworthy because although PFOA and PFOS are the most studied PFASs, shorter-chain molecules such as PFBS can still be toxic in humans and animals.[35,40] However, it is still important that such breakdown products be identified to completely understand the broader impact of PFASs and their remediation methods.

Future studies should focus on ensuring that the environmental conditions (amendments, temperature, moisture content) that mediated the complete breakdown of PFOS are replicable and suitable for soil samples from contaminated sites across the US. More field samples from a diverse selection of geographic locations should be obtained and exposed to eBeam technology in order to provide a more robust set of data. These experiments, if successful, would show that eBeam technology has even greater potential for site remediation of PFASs. Additionally, more experiments need to be designed specifically to elucidate the breakdown mechanisms of PFOA and PFOS. Obtaining this information would provide the opportunity to amend samples appropriately in order to achieve a more efficient breakdown of these chemicals.

Conclusions

This study was designed to improve upon the dose delivery of eBeam irradiation, allowing temperature to increase along with a continuous deposition of dose. We hypothesized that this method, along with amendments such as pH 13, would result in the complete breakdown of PFOS. The results showed complete breakdown of PFOS at all samples irradiated at 2000 kGy, as well as demonstrating the efficacy of this method in IDW soil samples low moisture content (10%) and pH 13. These results, though encouraging, are not yet sufficient for showing eBeam technology's applicability in all contaminated solid matrices. More studies with a wider variety of solid field samples as well as a focus on breakdown mechanisms should be performed in order to prove that

eBeam technology is suitable for *in situ* or pump-and-treat application for contaminated materials with diverse organic compositions.

CHAPTER V: CONCLUSIONS

This research aimed to identify and create the optimal conditions for complete breakdown of both PFOA and PFOS is liquid and solid matrices. The results indicate that PFOA can completely break down at a minimum dose of 50 kGy with the following amendments: additives $NaNO_3$ and $NaHCO_3$, pH 13, and anoxic conditions. PFOS can completely break down at 2000 kGy without amendments in water and at 10% moisture content and pH 13 in soil.

In these experiments, we proposed the use of electron beam (eBeam) technology as a means of destroying PFOA and PFOS in contaminated water and soil. This technology was chosen based partly on previous literature,[59,92] as well as its ability to deliver a consistent dose of ionizing radiation without much maintenance required once the proper dose has been determined (compared to exchanging spent GAC or fouled membrane filters).[3,12] eBeam has also been used as a means of treating other forms of contamination, including estrogenic compounds and heavy metals.[3,12] Based on these advantages, we decided to use eBeam technology to break down PFOA and PFOS. Initial studies were planned to examine the use of lower doses (10 kGy and 50 kGy) on lab-spiked water and sand samples. The findings led us to conclude that a 50 kGy dose of irradiation combined with NaNO3, NaHCO3, pH 13, and anoxic conditions were sufficient to fully break down PFOA. However, PFOS was not broken down more than ~40% using these means. Therefore, we concluded that higher doses of irradiation needed to be tested in order to elucidate the optimal conditions for PFOS breakdown.

A subsequent study was planned to investigate the effects of much higher doses of irradiation delivered in a continuous stream rather than in batches as in the Chapter III experiments. The same additives and conditions were tested at 500 kGy and 2000 kGy, with 2000 kGy being the more effective dose. It was also discovered that at the higher doses, additives actually hindered the breakdown process by preventing the desulfonation of PFOS.[90] Additionally, these results showed a direct relationship between increase in temperature and PFOS destruction. Breakdown exceeding 96% in PFOS was achieved in lab-spiked water and sand without additives.

Based on these findings, we decided to move forward with IDW soil samples collected from a contaminated site in Michigan, USA. To determine the importance of certain conditions for the reactions triggered by the irradiation, some of the samples were left in the state we received them in, while others were dried to a moisture content of 10% and adjusted to pH 13. The samples in the both groups showed statistically significant breakdown of both PFOA and PFOS, with those in the latter group yielding a complete breakdown of PFOS (>99.9%).

With these results in mind, several future studies still need to be performed in order to perfect the methods and determine the applicability of eBeam technology *in situ*. Firstly, any breakdown products created during the irradiation process must be identified. It is of utmost importance to confirm that this remediation method does not create new toxins. Secondly, confirming the exact breakdown mechanism will be invaluable in creating the optimal conditions for a variety of PFAS remediation applications. Elucidating the breakdown mechanisms of not only PFOA and PFOS, but

other major PFASs such as PFHpA will allow researchers to continue working towards remediating all PFASs. Another significant area of research is the combination of eBeam with other existing methods such as GAC. Although removal methods have already been successfully implemented for large-scale remediation, a current gap in literature is how combining methods such as GAC and AE resin with eBeam could improve the removal and/or destruction of PFASs. Lastly, the importance of scaling up the treatment to possibly remediate entire areas cannot be understated. As the overarching goal for all of this research has been to fully remediate PFAS-contaminated materials, future studies must include large-scale treatment.

The results of the low-dose and high-dose studies fill a gap in literature for a multi-faceted and robust method that is capable of completely breaking down both PFOA and PFOS in liquid and solid matrices. The widespread contamination of these chemicals as well as their inability to degrade naturally makes any non-toxic and effective breakdown method a valuable contribution to the field of PFAS remediation.

REFERENCES

(1) Giesy, J. P.; Kannan, K. Perfluorochemical Surfactants in the Environment. *Environmental Science and Technology*. April 1, 2002. https://doi.org/10.1021/es022253t.

(2) Verner, M. A.; Loccisano, A. E.; Morken, N. H.; Yoon, M.; Wu, H.; McDougall, R.; Maisonet, M.; Marcus, M.; Kishi, R.; Miyashita, C.; et al. Assfociations of Perfluoroalkyl Substances (PFAS) with Lower Birth Weight: An Evaluation of Potential Confounding by Glomerular Filtration Rate Using a Physiologically Based Pharmacokinetic Model (PBPK). *Environmental Health Perspectives* **2015**, *123* (12), 1317–1324. https://doi.org/10.1289/ehp.1408837.

(3) Wang, L.; Batchelor, B.; Pillai, S. D.; Botlaguduru, V. S. V. Electron Beam Treatment for Potable Water Reuse: Removal of Bromate and Perfluorooctanoic Acid. *Chemical Engineering Journal* **2016**, *302*, 58–68. https://doi.org/10.1016/j.cej.2016.05.034.

(4) Ma, S.; Xu, C.; Ma, J.; Wang, Z.; Zhang, Y.; Shu, Y.; Mo, X. Association between Perfluoroalkyl Substance Concentrations and Blood Pressure in Adolescents. *Environmental Pollution* **2019**, *254*. https://doi.org/10.1016/j.envpol.2019.112971.

(5) Luebker, D. J.; Hansen, K. J.; Bass, N. M.; Butenhoff, J. L.; Seacat, A. M. Interactions of Flurochemicals with Rat Liver Fatty Acid-Binding Protein. *Toxicology* **2002**, *176* (3), 175–185. https://doi.org/10.1016/S0300-483X(02)00081-1.

(6) Faithfull, N. S.; Weers, J. G. Perfluorocarbon Compounds. *Vox Sanguinis* **1998**, *74* (S2), 243–248. https://doi.org/10.1111/j.1423-0410.1998.tb05426.x.

(7) Fry, K.; Power, M. C. Persistent Organic Pollutants and Mortality in the United States, NHANES 1999–2011. *Environmental Health* **2017**, *16* (1), 105. https://doi.org/10.1186/s12940-017-0313-6.

(8) Pan, Y.; Shi, Y.; Wang, J.; Cai, Y. Evaluation of Perfluorinated Compounds in Seven Wastewater Treatment Plants in Beijing Urban Areas. *Science China Chemistry* **2011**, *54* (3), 552–558. https://doi.org/10.1007/s11426-010-4093-x.

(9) Zhang, Z.; Chen, J. J.; Lyu, X. J.; Yin, H.; Sheng, G. P. Complete Mineralization of Perfluorooctanoic Acid (PFOA) by γ-Irradiation in Aqueous Solution. *Scientific Reports* **2014**, *4*. https://doi.org/10.1038/srep07418.

(10) Kucharzyk, K. H.; Darlington, R.; Benotti, M.; Deeb, R.; Hawley, E. Novel Treatment Technologies for PFAS Compounds: A Critical Review. *Journal of Environmental Management* **2017**, *204*, 757–764. https://doi.org/10.1016/j.jenvman.2017.08.016.

(11) Woods, R.; AK, P. *Applied Radiation Chemistry: Radiation Processing.*; Wiley: New York City, 1994.

(12) Praveen, C.; Jesudhasan, P. R.; Reimers, R. S.; Pillai, S. D. Electron Beam Inactivation of Selected Microbial Pathogens and Indicator Organisms in Aerobically and Anaerobically Digested Sewage Sludge. *Bioresource Technology* **2013**, *144*, 652–657. https://doi.org/10.1016/j.biortech.2013.07.034.

(13) Nickelsen, M. G.; Cooper, W. J.; Lin, K.; Kurucz, C. N.; Waite, T. D. High Energy Electron Beam Generation of Oxidants for the Treatment of Benzene and Toluene in the Presence of Radical Scavengers. *Water Research* **1994**, *28* (5), 1227–1237. https://doi.org/10.1016/0043-1354(94)90211-9.

(14) Kurucz, C. N.; Waite, T. D.; Cooper, W. J.; Nickelsen, M. J. High Energy Electron Beam Irradiation of Water, Wastewater and Sludge; 1991; pp 1–43. https://doi.org/10.1007/978-1-4615-3392-4_1.

(15) Goldwhite, H. The Manhattan Project. *Journal of Fluorine Chemistry* **1986**, *33* (1–4), 109–132. https://doi.org/10.1016/S0022-1139(00)85273-2.

(16) Barlow, C. A.; Boyd, C. A.; Megan Kemp, C. J.; Kimberly Hoppe Parr, M. A.; Kemp, M. J.; Hoppe Parr, K. A. *PFAS Toxicology What Is Driving the Variation in Drinking Water Standards? Known for Excellence. Built on Trust. PFAS Toxicology-What Is Driving the Variation in Drinking Water Standards*; 2019.

(17) Giesy, J. P.; Kannan, K. Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science and Technology* **2001**, *35* (7), 1339–1342. https://doi.org/10.1021/es001834k.

(18) Milinovic, J.; Lacorte, S.; Vidal, M.; Rigol, A. Sorption Behaviour of Perfluoroalkyl Substances in Soils. *Science of the Total Environment* **2015**, *511*, 63–71. https://doi.org/10.1016/j.scitotenv.2014.12.017.

(19) Conder, J. M.; Hoke, R. A.; de Wolf, W.; Russell, M. H.; Buck, R. C. Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory

Criteria and Persistent Lipophilic Compounds. *Environmental Science and Technology*. February 15, 2008, pp 995–1003. https://doi.org/10.1021/es070895g.

(20) Hong, S.; Khim, J. S.; Wang, T.; Naile, J. E.; Park, J.; Kwon, B. O.; Song, S. J.; Ryu, J.; Codling, G.; Jones, P. D.; et al. Bioaccumulation Characteristics of Perfluoroalkyl Acids (PFAAs) in Coastal Organisms from the West Coast of South Korea. *Chemosphere* **2015**, *129*, 157–163. https://doi.org/10.1016/j.chemosphere.2014.06.023.

(21) Olsen, G. W.; Mair, D. C.; Lange, C. C.; Harrington, L. M.; Church, T. R.; Goldberg, C. L.; Herron, R. M.; Hanna, H.; Nobiletti, J. B.; Rios, J. A.; et al. Per- and Polyfluoroalkyl Substances (PFAS) in American Red Cross Adult Blood Donors, 2000–2015. *Environmental Research* **2017**, *157*, 87–95. https://doi.org/10.1016/j.envres.2017.05.013.

(22) Organofluorine Chemistry: Principles and Commercial Applications - Google Books https://books.google.com/books?hl=en&lr=&id=OW_1BwAAQBAJ&oi=fnd&pg=PA1&ots=Cdwcpjvpqo&sig=k1pXfmEC4B8D18DloZFJnW7UaNU#v=onepage&q&f=false (accessed Jan 20, 2020).

(23) Ignat'ev, N. v. Electrochemical Fluorination: A Powerful Tool for the Preparation of Organofluorine Compounds. In *Modern Synthesis Processes and Reactivity of Fluorinated Compounds: Progress in Fluorine Science*; Elsevier Inc., 2017; pp 71–123. https://doi.org/10.1016/B978-0-12-803740-9.00004-4.

(24) Okamura, S.; Katagiri, K. Chain Transfer to Telomer. *Die Makromolekulare Chemie* **1958**, *28* (1), 177–184. https://doi.org/10.1002/macp.1958.020280117.

(25) Boutevin, B.; Pietrasanta, Y. Telomerization. In *Comprehensive Polymer Science and Supplements*; Elsevier, 1989; pp 185–194. https://doi.org/10.1016/b978-0-08-096701-1.00076-8.

(26) Kissa, E. *Fluorinated Surfactants and Repellents (2nd Edition Revised and Expanded)*; Marcel Dekker, 2001.

(27) Boutevin, B. From Telomerization to Living Radical Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, *38* (18), 3235–3243. https://doi.org/10.1002/1099-0518(20000915)38:18<3235::AID-POLA20>3.0.CO;2-6.

(28) Berger, U.; Langlois, I.; Oehme, M.; Kallenborn, R. Comparison of Three Types of Mass Spectrometer for High-Performance Liquid Chromatography/Mass Spectrometry Analysis of Perfluoroalkylated Substances and Fluorotelomer Alcohols. *European Journal of Mass Spectrometry* **2004**, *10* (5), 579–588. https://doi.org/10.1255/ejms.679.

(29) Gebbink, W. A.; van Asseldonk, L.; van Leeuwen, S. P. J. Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands. *Environmental Science and Technology* **2017**, *51* (19), 11057–11065. https://doi.org/10.1021/acs.est.7b02488.

(30) O'Hagan, D. Understanding Organofluorine Chemistry. An Introduction to the C-F Bond. *Chemical Society Reviews* **2008**, *37* (2), 308–319. https://doi.org/10.1039/b711844a.

(31) Peters, D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *Solution Journal of Physical and Chemical Reference Data* **1963**, *38*, 1637. https://doi.org/10.1063/1.1733694.

(32) Giannetti, E. Thermal Stability and Bond Dissociation Energy of Fluorinated Polymers: A Critical Evaluation. *Journal of Fluorine Chemistry* **2005**, *126* (4), 623–630. https://doi.org/10.1016/j.jfluchem.2005.01.008.

(33) McClain, J. B.; McClain; Bryan, J. Characterization of Polymers and Amphiphiles in Liquid and Supercritical Carbon Dioxide. *PhDT* **2000**.

(34) Mastrantonio, M.; Bai, E.; Uccelli, R.; Cordiano, V.; Screpanti, A.; Crosignani, P. Drinking Water Contamination from Perfluoroalkyl Substances (PFAS): An Ecological Mortality Study in the Veneto Region, Italy. *European Journal of Public Health* **2018**, *28* (1), 180–185. https://doi.org/10.1093/eurpub/ckx066.

(35) Crebelli, R.; Caiola, S.; Conti, L.; Cordelli, E.; de Luca, G.; Dellatte, E.; Eleuteri, P.; Iacovella, N.; Leopardi, P.; Marcon, F.; et al. Can Sustained Exposure to PFAS Trigger a Genotoxic Response? A Comprehensive Genotoxicity Assessment in Mice after Subacute Oral Administration of PFOA and PFBA. *Regulatory Toxicology and Pharmacology* **2019**, *106*, 169–177. https://doi.org/10.1016/j.yrtph.2019.05.005.

(36) Bonefeld-Jorgensen, E. C.; Long, M.; Bossi, R.; Ayotte, P.; Asmund, G.; Krüger, T.; Ghisari, M.; Mulvad, G.; Kern, P.; Nzulumiki, P.; et al. Perfluorinated Compounds Are Related to Breast Cancer Risk in Greenlandic Inuit: A Case Control Study. *Environmental Health: A Global Access Science Source* **2011**, *10* (1). https://doi.org/10.1186/1476-069X-10-88.

(37) DeWitt, J. *Toxicological Effects of Perfluoroalkyl and Polyfluoroalkyl Substances*; Dietert, R. R., Ed.; Molecular and Integrative Toxicology; Springer International Publishing, 2015. https://doi.org/10.1007/978-3-319-15518-0.

(38) Barry, V.; Winquist, A.; Steenland, K. Perfluorooctanoic Acid (PFOA) Exposures and Incident Cancers among Adults Living Near a Chemical Plant. *Environmental Health Perspectives • 121*, 11–12. https://doi.org/10.1289/ehp.1306615.

(39) Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froelich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R. Half-Life of Serum Elimination of Perfluorooctanesulfonate, Perfluorohexanesulfonate, and Perfluorooctanoate in Retired Fluorochemical Production Workers. *Environmental Health Perspectives* **2007**, *115* (9), 1298–1305. https://doi.org/10.1289/ehp.10009.

(40) Eriksen, K. T.; Raaschou-Nielsen, O.; Sørensen, M.; Roursgaard, M.; Loft, S.; Møller, P. Genotoxic Potential of the Perfluorinated Chemicals PFOA, PFOS, PFBS, PFNA and PFHxA in Human HepG2 Cells. *Mutation Research - Genetic Toxicology and Environmental Mutagenesis* **2010**, *700* (1–2), 39–43. https://doi.org/10.1016/j.mrgentox.2010.04.024.

(41) Kennedy, G. L.; Symons, J. M. Carcinogenicity of Perfluoroalkyl Compounds; 2015; pp 265–304. https://doi.org/10.1007/978-3-319-15518-0_12.

(42) Kim, M. J.; Moon, S.; Oh, B. C.; Jung, D.; Ji, K.; Choi, K.; Park, Y. J. Association between Perfluoroalkyl Substances Exposure and Thyroid Function in Adults: A Meta-Analysis. *PLoS ONE* **2018**, *13* (5). https://doi.org/10.1371/journal.pone.0197244.

(43) Lewis, R.; Johns, L.; Meeker, J. Serum Biomarkers of Exposure to Perfluoroalkyl Substances in Relation to Serum Testosterone and Measures of Thyroid Function among Adults and Adolescents from NHANES 2011–2012. *International Journal of Environmental Research and Public Health* **2015**, *12* (6), 6098–6114. https://doi.org/10.3390/ijerph120606098.

(44) Shrestha, S.; Bloom, M. S.; Yucel, R.; Seegal, R. F.; Wu, Q.; Kannan, K.; Rej, R.; Fitzgerald, E. F. Perfluoroalkyl Substances and Thyroid Function in Older Adults. *Environment International* **2015**, *75*, 206–214. https://doi.org/10.1016/j.envint.2014.11.018.

(45) Min, J. Y.; Lee, K. J.; Park, J. B.; Min, K. B. Perfluorooctanoic Acid Exposure Is Associated with Elevated Homocysteine and Hypertension in US Adults. *Occupational and Environmental Medicine* **2012**, *69* (9), 658–662. https://doi.org/10.1136/oemed-2011-100288.

(46) Bao, W. W.; Qian, Z.; Geiger, S. D.; Liu, E.; Liu, Y.; Wang, S. Q.; Lawrence, W. R.; Yang, B. Y.; Hu, L. W.; Zeng, X. W.; et al. Gender-Specific Associations between Serum Isomers of Perfluoroalkyl Substances and Blood Pressure among

Chinese: Isomers of C8 Health Project in China. *Science of the Total Environment* **2017**, *607–608*, 1304–1312. https://doi.org/10.1016/j.scitotenv.2017.07.124.

(47) Holtcamp, W. Pregnancy-Induced Hypertension “Probably Linked” to PFOAcontamination. *Environmental Health Perspectives*. February 2012. https://doi.org/10.1289/ehp.120-a59.

(48) Johnson, P. I.; Sutton, P.; Atchley, D. S.; Koustas, E.; Lam, J.; Sen, S.; Robinson, K. A.; Axelrad, D. A.; Woodruff, T. J. The Navigation Guide—Evidence-Based Medicine Meets Environmental Health: Systematic Review of Human Evidence for PFOA Effects on Fetal Growth. *Environmental Health Perspectives*. Public Health Services, US Dept of Health and Human Services October 1, 2014, pp 1028–1039. https://doi.org/10.1289/ehp.1307893.

(49) Mondal, D.; Lopez-Espinosa, M. J.; Armstrong, B.; Stein, C. R.; Fletcher, T. Relationships of Perfluorooctanoate and Perfluorooctane Sulfonate Serum Concentrations between Mother-Child Pairs in a Population with Perfluorooctanoate Exposure from Drinking Water. *Environmental Health Perspectives* **2012**, *120* (5), 752–757. https://doi.org/10.1289/ehp.1104538.

(50) Lam, J.; Koustas, E.; Sutton, P.; Johnson, P. I.; Atchley, D. S.; Sen, S.; Robinson, K. A.; Axelrad, D. A.; Woodruff, T. J. The Navigation Guide—Evidence-Based Medicine Meets Environmental Health: Integration of Animal and Human Evidence for PFOA Effects on Fetal Growth. *Environmental Health Perspectives*. Public Health Services, US Dept of Health and Human Services October 1, 2014, pp 1040–1051. https://doi.org/10.1289/ehp.1307923.

(51) Smith, C. J.; Perfetti, T. A. An Approximated One-Quarter of IARC Group 3 (Unclassifiable) Chemicals Fit More Appropriately into IARC Group 4 (Probably Not Carcinogenic). *Toxicology Research and Application* **2019**, *3*, 239784731984064. https://doi.org/10.1177/2397847319840645.

(52) Abdellatif, A. G.; Préat, V.; Vamecq, J.; Nilsson, R.; Roberfroid, M. Peroxisome Proliferation and Modulation of Rat Liver Carcinogenesis by 2,4-Dichlorophenoxyacetic Acid, 2,4,5-Trichlorophenoxyacetic Acid, Perfluorooctanoic Acid and Nafenopin. *Carcinogenesis* **1990**, *11* (11), 1899–1902. https://doi.org/10.1093/carcin/11.11.1899.

(53) Ghisi, R.; Vamerali, T.; Manzetti, S. Accumulation of Perfluorinated Alkyl Substances (PFAS) in Agricultural Plants: A Review. *Environmental Research*. Academic Press Inc. February 1, 2019, pp 326–341. https://doi.org/10.1016/j.envres.2018.10.023.

(54) Haukås, M.; Berger, U.; Hop, H.; Gulliksen, B.; Gabrielsen, G. W. Bioaccumulation of Per- and Polyfluorinated Alkyl Substances (PFAS) in Selected Species from the Barents Sea Food Web. *Environmental Pollution* **2007**, *148* (1), 360–371. https://doi.org/10.1016/j.envpol.2006.09.021.

(55) Kwok, K. Y.; Yamazaki, E.; Yamashita, N.; Taniyasu, S.; Murphy, M. B.; Horii, Y.; Petrick, G.; Kallerborn, R.; Kannan, K.; Murano, K.; et al. Transport of Perfluoroalkyl Substances (PFAS) from an Arctic Glacier to Downstream Locations: Implications for Sources. *Science of the Total Environment* **2013**, *447*, 46–55. https://doi.org/10.1016/j.scitotenv.2012.10.091.

(56) Denys, S.; Fraize-Frontier, S.; Moussa, O.; Bizec, B. le; Veyrand, B.; Volatier, J. L. Is the Fresh Water Fish Consumption a Significant Determinant of the Internal Exposure to Perfluoroalkylated Substances (PFAS)? *Toxicology Letters* **2014**, *231* (2), 233–238. https://doi.org/10.1016/j.toxlet.2014.07.028.

(57) Berger, U.; Glynn, A.; Holmström, K. E.; Berglund, M.; Ankarberg, E. H.; Törnkvist, A. Fish Consumption as a Source of Human Exposure to Perfluorinated Alkyl Substances in Sweden - Analysis of Edible Fish from Lake Vättern and the Baltic Sea. *Chemosphere* **2009**, *76* (6), 799–804. https://doi.org/10.1016/j.chemosphere.2009.04.044.

(58) McCleaf, P.; Englund, S.; Östlund, A.; Lindegren, K.; Wiberg, K.; Ahrens, L. Removal Efficiency of Multiple Poly- and Perfluoroalkyl Substances (PFASs) in Drinking Water Using Granular Activated Carbon (GAC) and Anion Exchange (AE) Column Tests. *Water Research* **2017**, *120*, 77–87. https://doi.org/10.1016/j.watres.2017.04.057.

(59) Liu, C. J.; Werner, D.; Bellona, C. Removal of Per- And Polyfluoroalkyl Substances (PFASs) from Contaminated Groundwater Using Granular Activated Carbon: A Pilot-Scale Study with Breakthrough Modeling. *Environmental Science: Water Research and Technology* **2019**, *5* (11), 1844–1853. https://doi.org/10.1039/c9ew00349e.

(60) Codling, G.; Vogt, A.; Jones, P. D.; Wang, T.; Wang, P.; Lu, Y. L.; Corcoran, M.; Bonina, S.; Li, A.; Sturchio, N. C.; et al. Historical Trends of Inorganic and

Organic Fluorine in Sediments of Lake Michigan. *Chemosphere* **2014**, *114*, 203–209. https://doi.org/10.1016/j.chemosphere.2014.03.080.

(61) Bartell, S. M.; Calafat, A. M.; Lyu, C.; Kato, K.; Ryan, P. B.; Steenland, K. Rate of Decline in Serum PFOA Concentrations after Granular Activated Carbon Filtration at Two Public Water Systems in Ohio and West Virginia. *Environmental Health Perspectives* **2010**, *118* (2), 222–228. https://doi.org/10.1289/ehp.0901252.

(62) Deng, S.; Yu, Q.; Huang, J.; Yu, G. Removal of Perfluorooctane Sulfonate from Wastewater by Anion Exchange Resins: Effects of Resin Properties and Solution Chemistry. *Water Research* **2010**, *44* (18), 5188–5195. https://doi.org/10.1016/j.watres.2010.06.038.

(63) Appleman, T. D.; Dickenson, E. R. V.; Bellona, C.; Higgins, C. P. Nanofiltration and Granular Activated Carbon Treatment of Perfluoroalkyl Acids. *Journal of Hazardous Materials* **2013**, *260*, 740–746. https://doi.org/10.1016/j.jhazmat.2013.06.033.

(64) The cost of inaction: A socioeconomic analysis of environmental and health ... - Gretta Goldenman, Meena Fernandes, Michael Holland, Tugce Tugran, Amanda Nordin, Cindy Schoumacher, Alicia McNeill - Google Books https://books.google.com/books?hl=en&lr=&id=6uaVDwAAQBAJ&oi=fnd&pg=PA5&dq=PFAS+incineration&ots=Vol5TUezSC&sig=b_j89bfyTm7rGirwI5or8MlvyV0#v=onepage&q=PFAS%20incineration&f=false (accessed Jan 28, 2020).

(65) Bell, C.; Gentile, M.; Kalve, E.; Ross, I.; Horst, J.; Suthersan, S. *Emerging Contaminants Handbook*; 2019.

(66) Khan, M. Y.; So, S.; da Silva, G. Decomposition Kinetics of Perfluorinated Sulfonic Acids. *Chemosphere* **2020**, *238*, 124615. https://doi.org/10.1016/j.chemosphere.2019.124615.

(67) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Treatment Technologies for Aqueous Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA). https://doi.org/10.1007/s11783-009-0022-7.

(68) Darlington, R.; Barth, E.; McKernan, J. The Challenges of PFAS Remediation. *Military Engineer*. Society of American Military Engineers January 1, 2018, pp 58–60.

(69) Stratton, G. R.; Bellona, C. L.; Dai, F.; Holsen, T. M.; Thagard, S. M. Plasma-Based Water Treatment: Conception and Application of a New General Principle for Reactor Design. *Chemical Engineering Journal* **2015**, *273*, 543–550. https://doi.org/10.1016/j.cej.2015.03.059.

(70) Stratton, G. R.; Dai, F.; Bellona, C. L.; Holsen, T. M.; Dickenson, E. R. v.; Mededovic Thagard, S. Plasma-Based Water Treatment: Efficient Transformation of Perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater. *Environmental Science & Technology* **2017**, *51* (3), 1643–1648. https://doi.org/10.1021/acs.est.6b04215.

(71) Singh, R. K.; Fernando, S.; Baygi, S. F.; Multari, N.; Thagard, S. M.; Holsen, T. M. Breakdown Products from Perfluorinated Alkyl Substances (PFAS)

Degradation in a Plasma-Based Water Treatment Process. *Environmental Science & Technology* **2019**, *53* (5), 2731–2738. https://doi.org/10.1021/acs.est.8b07031.

(72) Pillai, S. D.; Shayanfar, S. Electron Beam Technology and Other Irradiation Technology Applications in the Food Industry. *Topics in Current Chemistry*. Springer Verlag February 1, 2017. https://doi.org/10.1007/s41061-016-0093-4.

(73) Kim, T. H.; Lee, S. H.; Kim, H. Y.; Doudrick, K.; Yu, S.; Kim, S. D. Decomposition of Perfluorooctane Sulfonate (PFOS) Using a Hybrid Process with Electron Beam and Chemical Oxidants. *Chemical Engineering Journal* **2019**, *361*, 1363–1370. https://doi.org/10.1016/j.cej.2018.10.195.

(74) Chmielewski, A. G. *AP/INT-03 Electron Beam Processing-What Are the Limits*.

(75) Pillai, S. D.; Shayanfar, S. Electron Beam Technology and Other Irradiation Technology Applications in the Food Industry; Springer, Cham, 2017; pp 249–268. https://doi.org/10.1007/978-3-319-54145-7_9.

(76) Gehringer, P.; Fiedler, H. Design of a Combined Ozone/Electron Beam Process for Waste Water and Economic Feasibility of the Process. In *Radiation Physics and Chemistry*; 1998; Vol. 52, pp 345–349. https://doi.org/10.1016/S0969-806X(98)00031-0.

(77) Hanssen, L.; Dudarev, A. A.; Huber, S.; Odland, J. Ø.; Nieboer, E.; Sandanger, T. M. Partition of Perfluoroalkyl Substances (PFASs) in Whole Blood and Plasma, Assessed in Maternal and Umbilical Cord Samples from Inhabitants of Arctic Russia and Uzbekistan. *Science of the Total Environment* **2013**, *447*, 430–437. https://doi.org/10.1016/j.scitotenv.2013.01.029.

(78) Woodard, S.; Berry, J.; Newman, B. Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. *Remediation Journal* **2017**, *27* (3), 19–27. https://doi.org/10.1002/rem.21515.

(79) Jeirani, Z.; Niu, C. H.; Soltan, J. Adsorption of Emerging Pollutants on Activated Carbon. *Reviews in Chemical Engineering* **2017**, *33* (5), 491–522. https://doi.org/10.1515/revce-2016-0027.

(80) Brasquet, C.; le Cloirec, P. Adsorption onto Activated Carbon Fibers: Application to Water and Air Treatments. *Carbon* **1997**, *35* (9), 1307–1313. https://doi.org/10.1016/S0008-6223(97)00079-1.

(81) Stratton, G. R.; Dai, F.; Bellona, C. L.; Holsen, T. M.; Dickenson, E. R. v.; Mededovic Thagard, S. Plasma-Based Water Treatment: Efficient Transformation of Perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater. *Environmental Science & Technology* **2017**, *51* (3), 1643–1648. https://doi.org/10.1021/acs.est.6b04215.

(82) Arias Espana, V. A.; Mallavarapu, M.; Naidu, R. Treatment Technologies for Aqueous Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA): A Critical Review with an Emphasis on Field Testing. *Environmental Technology and Innovation*. Elsevier October 1, 2015, pp 168–181. https://doi.org/10.1016/j.eti.2015.06.001.

(83) Ma, S. H.; Wu, M. H.; Tang, L.; Sun, R.; Zang, C.; Xiang, J. J.; Yang, X. X.; Li, X.; Xu, G. EB Degradation of Perfluorooctanoic Acid and Perfluorooctane

Sulfonate in Aqueous Solution. *Nuclear Science and Techniques* **2017**, *28* (9). https://doi.org/10.1007/s41365-017-0278-8.

(84) Gellrich, V.; Stahl, T.; Knepper, T. P. Behavior of Perfluorinated Compounds in Soils during Leaching Experiments. *Chemosphere* **2012**, *87* (9), 1052–1056. https://doi.org/10.1016/j.chemosphere.2012.02.011.

(85) Ahrens, L.; Yamashita, N.; Yeung, L. W. Y.; Taniyasu, S.; Horii, Y.; Lam, P. K. S.; Ebinghaus, R. Partitioning Behavior of Per- and Polyfluoroalkyl Compounds between Pore Water and Sediment in Two Sediment Cores from Tokyo Bay, Japan. *Environmental Science and Technology* **2009**, *43* (18), 6969–6975. https://doi.org/10.1021/es901213s.

(86) Darlington, R.; Barth, E.; McKernan, John. The Challenges of PFAS Remediation. *The Military Engineer* **2018**, *110*, 58–60.

(87) Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Thelakkat Kochunarayanan, P.; Kalve, E.; Hurst, J.; S. Dasgupta, S.; Burdick, J. A Review of Emerging Technologies for Remediation of PFASs. *Remediation* **2018**, *28* (2), 101–126. https://doi.org/10.1002/rem.21553.

(88) Trojanowicz, M.; Bartosiewicz, I.; Bojanowska-Czajka, A.; Szreder, T.; Bobrowski, K.; Nałęcz-Jawecki, G.; Męczyńska-Wielgosz, S.; Nichipor, H. Application of Ionizing Radiation in Decomposition of Perfluorooctane Sulfonate (PFOS) in Aqueous Solutions. *Chemical Engineering Journal* **2020**, *379*, 122303. https://doi.org/10.1016/j.cej.2019.122303.

(89) Feldheim, D. L.; Lawson, D. R.; Martin, C. R. Influence of the Sulfonate Countercation on the Thermal Stability of Nafion Perfluorosulfonate Membranes. *Journal of Polymer Science Part B: Polymer Physics* **1993**, *31* (8), 953–957. https://doi.org/10.1002/polb.1993.090310805.

(90) Miller, S. C. Profiling Sulfonate Ester Stability: Identification of Complementary Protecting Groups for Sulfonates. *J. Org. Chem* **2010**, *75*, 4632–4635. https://doi.org/10.1021/jo1007338.

(91) Hagen, D. F.; Belisle, J.; Johnson, J. D.; Venkateswarlu, P. Characterization of Fluorinated Metabolites by a Gas Chromatographic-Helium Microwave Plasma Detector-The Biotransformation of 1H,1H,2H,2H-Perfluorodecanol to Perfluorooctanoate. *Analytical Biochemistry* **1981**, *118* (2), 336–343. https://doi.org/10.1016/0003-2697(81)90591-1.

(92) Tang, C. Y.; Fu, Q. S.; Criddle, C. S.; Leckie, J. O. Effect of Flux (Transmembrane Pressure) and Membrane Properties on Fouling and Rejection of Reverse Osmosis and Nanofiltration Membranes Treating Perfluorooctane Sulfonate Containing Wastewater. *Environmental Science and Technology* **2007**, *41* (6), 2008–2014. https://doi.org/10.1021/es062052f.